

Randomly crosslinked macromolecular systems: vulcanization transition to and properties of the amorphous solid state

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[Received 21 September 1995 and accepted 10 January 1996]

Abstract

As Charles Goodyear discovered in 1839, when he first vulcanized rubber, a macromolecular liquid is transformed into a solid when a sufficient density of permanent crosslinks is introduced at random. At this continuous equilibrium phase transition, the liquid state, in which all macromolecules are delocalized, is transformed into a solid state, in which a non-zero fraction of macromolecules have spontaneously become localized. This solid state is a most unusual one: localization occurs about mean positions that are distributed homogeneously and randomly, and to an extent that varies randomly from monomer to monomer. Thus, the solid state emerging at the vulcanization transition is an *equilibrium amorphous solid state*: it is properly viewed as a solid state that bears the same relationship to the liquid and crystalline states as the spin glass state of certain magnetic systems bears to the paramagnetic and ferromagnetic states, in the sense that, like the spin glass state, it is diagnosed by a subtle order parameter.

In this article we give a detailed exposition of a theoretical approach to the physical properties of systems of randomly, permanently crosslinked macromolecules. Our primary focus is on the equilibrium properties of such systems, especially in the regime of Goodyear's vulcanization transition. This approach rests firmly on techniques from the statistical mechanics of disordered systems pioneered by Edwards and co-workers in the context of macromolecular systems, and by Edwards and Anderson in the context of magnetic systems. We begin with a review of the semi-microscopic formulation of the statistical mechanics of randomly crosslinked macromolecular systems due to Edwards and co-workers, in particular discussing the role of crosslinks as quenched random variables. Then we turn to the issue of order parameters, and review a version capable, *inter alia*, of diagnosing the amorphous solid state. To develop some intuition, we examine the order parameter in an idealized situation, which subsequently turns out to be surprisingly relevant. Thus, we are motivated to hypothesize an explicit form for the order parameter in the amorphous solid state that is parametrized in terms of two physical quantities: the fraction of localized monomers, and the statistical distribution of localization lengths of localized monomers. Next, we review the symmetry properties of the system itself, the liquid state and the amorphous solid state, and discuss connections with scattering experiments. Then, we review a representation of the statistical mechanics of randomly crosslinked macromolecular systems from which the quenched disorder has been eliminated via an application of the replica technique. We transform the statistical mechanics into a field-theoretic representation, which exhibits a close connection with the order parameter, and analyse this representation at the saddle-point level. This analysis reveals that sufficient crosslinking causes an instability of the liquid state, this state giving way to the amorphous solid state. To address the properties of the

amorphous solid state itself, we solve the self-consistent equation for the order parameter by adopting the hypothesis discussed earlier. Hence, we find that the vulcanization transition is marked by the appearance of a non-zero fraction of localized monomers, which we compute, the dependence of this fraction on the crosslink density indicating a connection with random graph theory and percolation. We also compute the distribution of localization lengths that characterizes the ordered state, which we find to be expressible in terms of a universal scaling function of a single variable, at least in the vicinity of the transition. Finally, we analyse the consequences of incorporating a certain specific class of correlations associated with the excluded-volume interaction.

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There is probably no other inert substance, the properties of which excite in the human mind, when first called to examine it, an equal amount of curiosity, surprise, and admiration. Who can examine, and reflect upon [the properties of] gum-elastic, without adoring the wisdom of the Creator?

Charles Goodyear, *Gum-Elastic and its Varieties, with a Detailed Account of its Applications and Uses, and of the Discovery of Vulcanization* (1855).

1. Introduction and overview

In this article we aim to present a theoretical description of the physical properties of systems of macromolecules that have been randomly and permanently crosslinked. Our focus will be on the equilibrium properties of such systems, especially in the regime of the vulcanization transition. By the term vulcanization transition we mean the sharp thermodynamic phase transition occurring when the mean density of crosslinks exceeds a certain critical value. At this critical crosslink-density, the equilibrium state of the system undergoes a continuous transition: for subcritical values the equilibrium state is a liquid state, in which all the macromolecules are delocalized; for supercritical values the equilibrium state is an amorphous solid state, in which a non-zero fraction of macromolecules form a macroscopic network, and spontaneously become localized, albeit about certain random locations. Thus, our focus will be on the spontaneous emergence of the equilibrium amorphous solid state at the vulcanization transition, and the consequent properties of this unusual state.

It must be emphasized at the outset that the theoretical description of the vulcanization transition to and properties of the amorphous solid state of randomly crosslinked macromolecular networks presented here represents the confluence of two pioneering contributions to the theory of condensed matter: the Deam–Edwards theory of a single crosslinked macromolecule [1], and the Edwards–Anderson theory of spin glasses [2].

The basic ingredients of the present approach to the physical properties of randomly crosslinked macromolecular networks are as follows. We adopt a semi-microscopic description of the macromolecules, in which the detailed microscopic chemistry of the macromolecules and solvent (if any there be) feature only to the

extent that they determine the following effective parameters: the total arclength of each macromolecule, the persistence length (i.e. the length of the statistically independent macromolecular segments, which we term monomers), and the excluded-volume strength (i.e. the parameter that describes the effective repulsion between monomers). Thus, we regard the macromolecules as extended, featureless, flexible linear objects, each capable of exhibiting a large number of configurations, and use classical equilibrium statistical mechanics to address the properties of systems composed of a thermodynamically large number of such macromolecules. We regard the crosslinks as permanent elements that constrain certain randomly chosen monomers to remain adjacent to one another. Thus the crosslinked macromolecular system is a system with quenched disorder, in the sense that in addition to the macromolecular freedoms—the so-called annealed variables, which undergo equilibrium statistical-mechanical fluctuations—there are additional variables, those that specify the detailed realization of the crosslinking, that do not undergo equilibrium statistical-mechanical fluctuations. Instead, these variables—the so-called quenched random variables—vary only between realizations of the physical system. We treat these quenched random variables statistically, too, but account for their quenched nature by invoking the replica technique.

We now give an overview of our basic strategy for determining the physical properties of randomly crosslinked macromolecular networks.

We characterize the plausible equilibrium states of the system—liquid, globule, crystalline solid, amorphous solid—in terms of an order parameter, designed to discriminate between these states. This order parameter is a vastly more intricate object than the order parameters that arise, say, in the study of ferromagnetism or even spin glasses, and one must explore enormously larger spaces to find its equilibrium value. By investigating a simple caricature of the amorphous solid state we are, however, able to identify a physically well-motivated scheme for parametrizing the amorphous solid state order parameter at a manageable level: via a single number—the fraction of spatially localized monomers—and a normalized probability distribution—the statistical distribution of localization lengths of the localized monomers.

We focus on the free energy and the order parameter for the system of interacting macromolecular freedoms subject to the crosslinking constraints. Application of the replica technique to these quantities allows for the elimination of the quenched random variables; the price for this elimination is the introduction of an unusual and rather complicated effective coupling amongst the replicated macromolecular freedoms. Our scheme for parametrizing the order parameter leaves intact the permutation symmetry amongst the replicas. Next, we introduce a certain stochastic field, the argument of which is replicated (real or wavevector) space, via which we transform the replicated macromolecular description into a field-theoretic one. In this representation, the individual macromolecules are coupled to one another only indirectly, via their coupling to the fluctuations of the stochastic field, although the replicas of any given macromolecule remain directly coupled to each other. Via the introduction of a suitable external potential we demonstrate the connection between the order parameter and the stochastic field.

In order to elucidate the physical properties of the system we adopt a mean-field approach, which amounts to our approximating, via the saddle-point method, the averages over the stochastic field in the field-theoretical expressions for the free energy and order parameter. The state of the physical system then follows from the

form of the appropriate stationary value of the stochastic field or, equivalently, from the form of the self-consistent value of the order parameter. For mean crosslink densities smaller than a certain critical value, of order one crosslink per macromolecule, there is only one stationary value, which is elementary, and the corresponding state is the liquid state. For supercritical crosslink densities the appropriate stationary value is most definitely not elementary, and the corresponding state is the amorphous solid state. At the critical crosslink density the system undergoes a continuous vulcanization transition from the liquid state to the amorphous solid state.

To determine the properties of the amorphous solid state itself, we hypothesize that the self-consistent value of the order parameter lies within the family of order-parameter values reachable via our (severely restrictive but nevertheless physically plausible) parametrization. Quite remarkably, this is indeed the case: our parametrization does not merely yield a variational approximation to the amorphous solid state. Instead, although one has no *a priori* reason to suppose that it should, it permits an *exact* mean-field description of randomly crosslinked macromolecular networks to be constructed. What emerges is an amorphous solid state characterized by a non-zero fraction of localized monomers. The precise value of this fraction depends on the crosslink density, and vanishes continuously at the transition and in the liquid state. This fraction depends on the crosslink density in a manner identical to that found in random graph theory and percolation. The state is further characterized by a crosslink-density-dependent distribution of localization lengths, which quantifies the manner in which the localized monomers have become localized around their random mean positions. The typical localization length diverges continuously at the transition and in the liquid state. In the vicinity of the transition, the distribution of localization lengths has a scaling form governed by a universal function, which we compute. To date, we have been unable to obtain conclusive results for the distribution of localization lengths far from the amorphous solidification transition. The reason for this is purely technical: at a certain stage in the development we employ a perturbative calculation, in which the small parameter is the characteristic inverse localization length, measured in units of the radius of gyration of a single, non-interacting macromolecule, this parameter being zero in the liquid state, and small in the amorphous solid state only in the vicinity of the transition.

In addition to developing a purely mean-field description of the transition to and properties of the amorphous solid state, we incorporate a class of correlations associated with the excluded-volume interactions. We accomplish this by treating a certain sector of the stochastic field at the Gaussian level, rather than the saddle-point level. What emerges from this treatment is merely a particularly simple finite renormalization of a specific parameter of the mean-field theory, at least in three spatial dimensions.

Approaches based on percolation theory [3] are sometimes pursued in the context of the modelling of randomly crosslinked macromolecular networks; see [4]. However, such approaches entail only a single statistical ensemble, and hence cannot treat the equilibration of thermal (i.e. annealed) freedoms in the presence of quenched freedoms (crosslinks, in the present case). If the percolation ensemble is interpreted as describing the quenched freedoms then it can account for the appearance of an infinite network at a critical crosslink density, but it cannot account for the thermal fluctuations, which determine the physical properties of the

liquid and amorphous solid states. In particular the degree of localization in the amorphous solid state and the entropic elasticity of the network cannot be calculated from first principles in a percolation-based model, which does not distinguish between thermal and quenched freedoms. If, on the other hand, the percolation ensemble is interpreted as describing the thermal fluctuations of the macromolecular freedoms then it may serve as a model for chemical gelation, in which crosslinks continuously form and break up, but it cannot account for permanent, quenched crosslinks.

An approach to the properties of randomly permanently crosslinked macromolecular systems that accounts for both thermal fluctuations and quenched disorder has been introduced by Edwards and co-workers [1, 6, 7]. In addition to formulating the statistical mechanics of a single randomly crosslinked macromolecule using the replica technique, Deam and Edwards investigated the elastic properties of the system by invoking a variational method [1]. Ball and Edwards investigated the incorporation of correlations, and Ball also studied certain aspects of many-macromolecule systems [7].

The point of view that the solid state of randomly crosslinked macromolecular networks represents an unusual, equilibrium amorphous solid state of matter was introduced and developed in detail in [8–11]. In addition, the order parameter appropriate for detecting this amorphous solid state was introduced and explained in these papers, and the instability of the liquid state with respect to the formation of an amorphous solid, induced by sufficient crosslinking, was also identified there. Extending these ideas, the transition to and certain properties of the amorphous solid state, including its elastic properties, were obtained within the context of a variational mean-field approach in [12]. This variational approach was improved through an exact mean-field approach, the central elements of which were reported in [13]. The present article is intended to provide a fairly complete exposition of this approach to the statistical mechanics of randomly crosslinked macromolecular networks, including a detailed account of the work reported in [12, 13].

By adopting the Deam–Edwards approach [1] and the amorphous solid order parameter picture of [8, 9], Panyukov has made a number of contributions to the theory of well-crosslinked macromolecular networks [14]. To accomplish these, he considers a single linear macromolecule, randomly crosslinked, which is intended to represent a physical network of many randomly crosslinked macromolecules. These contributions, which are reviewed in [15], are based on the introduction of a well-known free-field representation of a random walk [16], the resulting field being treated at the mean-field level, along with an additional replica limit. Focusing, as it does, on the statistical mechanics of a single, well-crosslinked macromolecule, Panyukov's approach is unsuitable for developing a theory of the transition between the liquid and amorphous solid states, which occurs at crosslink densities of order one per macromolecule.

The present approach to the physics of randomly crosslinked macromolecular systems possesses the following distinctive virtues. First, both thermal freedoms (i.e. the macromolecular positions) and quenched freedoms (i.e. the crosslink locations) are incorporated, and handled appropriately, in contrast with percolative pictures. The replica technique provides the tool for accomplishing this. In fact, the percolative picture emerges from the present approach in the form of statistical information concerning the presence of localized macromolecules. However, the present approach is considerably richer, additionally yielding statistical-mechanical

information about the (thermally fluctuating) macromolecular system. In particular, it allows a unified treatment of liquid and amorphous solid states. Second, the physical many-macromolecule character of the system is maintained, in contrast with approaches that consider instead the properties of a single macromolecule. This is particularly significant, especially in the vicinity of the solidification transition, where the number of physical crosslinks is of order one per macromolecule, and allows us to develop a theory of the solidification transition. Third, the present approach leads directly to an order parameter for the amorphous solid state, which is related to that of spin glass physics. The order parameter has a natural, physical interpretation, which facilitates the hypothesizing of an appropriate form for it. Fourth, the physical freedoms, namely the macromolecular configurations, appear directly throughout the development, not being exchanged for some problem-specific formal representation. We can, therefore, be confident that the macromolecular character of the system is retained, especially when approximations are made. Indeed, the entire approach is very robust, so that, in addition to being of interest in the context of vulcanized macromolecular systems, it can readily be extended to address a wide range of other physical systems, such as crosslinked manifolds [29], endlinked systems of flexible, semi-flexible and rigid macromolecules [73], continuous random network models of structural glasses [70], and proteins. In addition, it should prove possible to extend the present approach to address issues of dynamics. Moreover, looking beyond the algebraic details, one sees a theoretical superstructure that is rather natural, direct and perhaps even conventional, at least from the point of view of statistical field theory. Fifth, the use of the present approach has primarily been restricted to the mean-field level of approximation. However, it is not a variational mean-field theory: instead the relevant saddle-point is determined exactly. This makes the approach a particularly promising starting point for future developments, such as the elucidation of the elastic properties and of the role of thermal fluctuations. It should be mentioned that the full stability of the saddle-point that we have determined has not yet been established. One current shortcoming of the present approach arises from the technical difficulty of computing properties in the regime of high crosslinking (e.g. deep in the amorphous solid state). This does not limit the scope of our primary aim, viz to explore the vicinity of the transition to the amorphous solid state. A second shortcoming is the inability of the approach, at least in its present formulation, to respect the interlocking of closed loops of macromolecules (discussed in section 2.2) that crosslinking can induce.

The present article is organized as follows. In the present, introductory, section we provide an overview of the article. In section 2 we discuss the basic elements of the model of macromolecular systems on which the present approach is based, including the level of description of macromolecular configurations, the Edwards measure for their statistical weights, and the notion of crosslinks as quenched random variables. We also discuss the partition function, free energy and issues of indistinguishability, along with the statistical characterization of the crosslinks, and the notion of disorder averages of certain physically relevant quantities. In section 3 we develop the general subject of order parameters appropriate for the amorphous solid and other states, discussing the properties that such order parameters should possess. We explore a simple scenario for the amorphous solid state, which provides physical motivation for a certain specific hypothesis that we make for the form taken by the amorphous solid order parameter in the amorphous solid state. At this stage we introduce the concept of gel and sol fractions and the statistical distribution of

localization lengths associated with localized monomers. We also analyse the symmetry properties of the ordered state, and discuss the connection between the order parameter and the elastic scattering of neutrons. In section 4 we address the statistical mechanics of randomly crosslinked macromolecular networks, invoking the replica technique in order to eliminate the (quenched random) crosslink variables. We also introduce a suitable replica-Helmholtz free energy, which is dependent on a convenient generalized external potential. In section 5 we reformulate the statistical mechanics of randomly crosslinked macromolecular networks in field-theoretic terms by introducing a certain stochastic field, which is closely related to the amorphous solid state order parameter. In section 6 we explore the properties of the resulting field theory within the context of a natural mean-field approximation. We exhibit the instability of the liquid state, and we compute the free energy and self-consistent order parameter in the vicinity of the transition. We also describe the characteristics of the amorphous solid state that emerge from this approach. In section 7 we incorporate certain correlations associated with density-sector fluctuations, and demonstrate that the results of the previous sections of this article are robust with respect to the incorporation of these fluctuations. In section 8 we make some concluding remarks. We have organized this article so that the main text is, to a large degree, unencumbered by lengthy mathematical details. Wherever possible such details have been relegated to one of eleven appendices, in which we demonstrate in full detail how the results of the main text are established.

Perhaps the most significant property to emerge at the vulcanization transition is rigidity with respect to shear deformations, i.e. elasticity. We are currently extending the present work to include the elastic properties of the amorphous solid state of randomly crosslinked macromolecular networks [17].

2. Model of the macromolecular system

2.1. Macromolecular system prior to crosslinking

We consider a system consisting of a large number N of long, flexible macromolecules, initially identical, and contained in a large d -dimensional hypercube of volume V . The macromolecules are characterized by their common arclength L and (weakly temperature-dependent) persistence length ℓ ($\ell \ll L$), so that the number of effectively statistically independent segments comprising each macromolecule is of order $L/\ell \gg 1$. Semi-microscopic spatial configurations of the system are characterized by the collection of spatial configurations of the macromolecules $\{\mathbf{R}_i(\sigma)\}_{i=1}^N$, in which $\mathbf{R}_i(\sigma)$ is the d -dimensional position vector of the monomer an arclength distance σ from a specific end of macromolecule i , the (discrete) macromolecule index i ranging from 1 to N and the (continuous) arclength variable σ ranging from 0 to L .

It is convenient to exchange the dimensionful position vector \mathbf{R} and arclength σ for dimensionless versions \mathbf{c} and s via the transformation

$$\mathbf{R}_i(\sigma) \equiv (\ell L/d)^{1/2} \mathbf{c}_i(s), \quad (2.1 a)$$

$$\sigma \equiv Ls. \quad (2.1 b)$$

Thus, we shall be measuring spatial distances in units of $(\ell L/d)^{1/2}$ (i.e. the root mean squared end-to-end distance of a free macromolecule divided by \sqrt{d}), and arclength distances in units of the total arclength L . We shall measure energies in units such that $k_B T$ is unity.

At the level of the present semi-microscopic description, and prior to the incorporation of the effects of either monomer–monomer interactions or crosslinks, we account for the connectivity of the constituent macromolecules by adopting the Wiener measure [18–20], in terms of which the statistical weight [21] of the configuration of the system $\{\mathbf{c}_i(s)\}_{i=1}^N$ is proportional to $\exp(-H_1^W)$, where

$$H_1^W \equiv \frac{1}{2} \sum_{i=1}^N \int_0^1 ds \left| \frac{d}{ds} \mathbf{c}_i(s) \right|^2. \quad (2.2)$$

The subscript 1 on H_1^W anticipates the introduction of replicas of the system, which we shall need to make below. We shall often need to consider normalized expectation values taken with respect to the Wiener measure, which we shall denote by the angle-bracket pair $\langle \dots \rangle_1^W$, defined by

$$\langle \dots \rangle_1^W \equiv \frac{\int \mathcal{D}\mathbf{c} \exp(-H_1^W) \dots}{\int \mathcal{D}\mathbf{c} \exp(-H_1^W)}, \quad (2.3)$$

where the dots represent an arbitrary function of the configuration of the system, and the measure

$$\mathcal{D}\mathbf{c} \equiv \prod_{i=1}^N \prod_{0 \leq s \leq 1} d\mathbf{c}_i(s) \quad (2.4)$$

indicates functional integration over all spatial configurations of the system, i.e. over all configurations of the N macromolecules. The subscript 1 on $\langle \dots \rangle_1^W$ also indicates that the average is taken only over the configurations of a single copy of the system, also anticipating the introduction of replicas.

We account for monomer–monomer interactions in a phenomenological manner, by augmenting the Wiener measure with an additional factor that has the effect of suppressing the statistical weight of configurations in which pairs of monomers occupy common regions of space [18–20]. To this end, we replace the Wiener measure, equation (2.2), by the Edwards measure, in terms of which the statistical weight of the configuration $\{\mathbf{c}_i(s)\}_{i=1}^N$ is proportional to $\exp(-H_1^E)$, where

$$H_1^E = \frac{1}{2} \sum_{i=1}^N \int_0^1 ds \left| \frac{d}{ds} \mathbf{c}_i(s) \right|^2 + \frac{\lambda^2}{2} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \delta^{(d)}(\mathbf{c}_i(s) - \mathbf{c}_{i'}(s')). \quad (2.5)$$

Here, $\delta^{(d)}(\mathbf{c})$ is the d -dimensional Dirac δ -function, and the dimensionless (real, positive) parameter λ^2 characterizes the strength of the suppression of statistical weight due to the (repulsive) excluded-volume interaction between monomers [18–20]. The excluded-volume interaction is suitably modified so as to exclude interactions between adjacent monomers on a common macromolecule (i.e. monomers for which $|s - s'| < \ell/L$). The expression for the Edwards measure in terms of dimensionful variables is given in [22]. The system can be regarded as a melt of macromolecules, in which case the interaction parameter λ^2 is intended to account for the monomer–monomer interaction. Alternatively, it can be regarded as a solution of macromolecules dissolved in a good solvent, in which case λ^2 is intended to represent the effective monomer–monomer interaction (i.e. the bare interaction renormalized by the monomer–solvent and solvent–solvent interactions, the solvent degrees of freedom having been integrated out). In both cases, λ^2 is weakly temperature dependent. Even at the level of mean-field theory, the excluded-volume

interaction plays a crucial role: it partially compensates the effective monomer–monomer attraction due to the crosslinks in just such a fashion as to maintain the macroscopic homogeneity of the system whilst allowing for the possibility of transition from the liquid to the amorphous solid state.

We shall need to consider normalized expectation values taken with respect to the Edwards measure, which we shall denote by the angle-bracket pair $\langle \dots \rangle_1^E$, defined by

$$\langle \dots \rangle_1^E \equiv \frac{\int \mathcal{D}\mathbf{c} \exp(-H_1^E) \dots}{\int \mathcal{D}\mathbf{c} \exp(-H_1^E)}, \quad (2.6)$$

where the dots represent an arbitrary function of the configuration of the system, and once again $\mathcal{D}\mathbf{c}$ indicates functional integration over all configurations of the system. Again, the subscripts 1 on H_1^E and $\langle \dots \rangle_1^E$ anticipate the introduction of replicas.

It should be noted that neither the Wiener measure nor the Edwards measure explicitly breaks translational or rotational symmetry: the statistical weight of a configuration remains unchanged if all the monomers are simultaneously translated through a common amount or rotated through a common angle about a common axis.

2.2. Crosslinks as quenched random variables

Our aim is to address the statistical mechanics of thermodynamically large systems of macromolecules into which a large number of crosslinks have been permanently introduced at random. Each crosslink has the effect of constraining two randomly selected monomers, the locations of which were kinematically independent prior to the introduction of the crosslink, to occupy a common spatial location. Thus the effect of the crosslinks is to eliminate from the ensemble of configurations of the system all configurations that do not obey the entire set of random constraints enforced by the crosslinks. Our task is therefore to address the statistical mechanics of macromolecular systems in the presence of a large number of random constraints.

A specific realization of the crosslinking is fully described by specifying which randomly selected pairs of monomers are connected by each crosslink, i.e. that the crosslink labelled by the index e serves to connect the monomer at arclength s_e on macromolecule i_e to the monomer at arclength s'_e on macromolecule i'_e , for $e = 1, \dots, M$, with M being the total number of crosslinks. Thus, only those configurations that satisfy the constraints

$$\mathbf{c}_{i_e}(s_e) = \mathbf{c}_{i'_e}(s'_e), \quad (\text{with } e = 1, \dots, M), \quad (2.7)$$

are retained in the ensemble. It should be noted that these constraints do not explicitly break translational symmetry.

In principle, of course, neither the crosslinks nor the integrity of the macromolecules are truly permanent. However, in many physical realizations of crosslinked macromolecular systems there is a very wide separation between the time-scale required for the crosslink-constrained macromolecular system to relax to a state of thermodynamic equilibrium and the much longer time-scale required for either the crosslinks or the macromolecules to break. For such systems, and it is such systems that we have in mind, the crosslinks and the macromolecules should be regarded as permanent, so that the number and identity of the monomers participating in crosslinks, $\{i_e, s_e; i'_e, s'_e\}_{e=1}^M$, should be treated as non-equilibrating

(i.e. quenched) random variables. The unconstrained macromolecular freedoms are regarded as reaching equilibrium in the presence of fixed values of the quenched variables. Thus, it is a meaningful task to address the equilibrium statistical mechanics of permanently crosslinked macromolecular systems.

It should be remarked that the relative statistical weights of the configurations that do satisfy the crosslinking constraints are hypothesized, at least *a priori*, to be unaffected by the introduction of crosslinks. That is, the statistical weights are proportional to $\exp(-H_1^E)$ for configurations satisfying the crosslinks and zero otherwise. However, as we shall see in detail below, for a sufficiently large density of crosslinks the translational and rotational symmetry of the equilibrium state of the system is spontaneously broken. That is, in a given (pure) state the statistical weights of configurations that are translations and rotations of one another are no longer identical, and thus localization can arise. Indeed, only one member of a family of translated and rotated configurations has a non-zero weight in a given (pure) state. The associated transition to an amorphous solid state is precisely the transition on which we are focusing. We remark that in the present context of amorphous solidification, translational and rotational symmetry are spontaneously broken in an unusual sense, in that they remain fully intact at the macroscopic level.

A second mechanism that leads to the violation of the hypothesis mentioned in the previous paragraph arises because sufficient crosslinking is liable to give a topological character to the system of macromolecules, at least in three spatial dimensions, in the sense that for a given set of crosslinks there will be families of configurations allowed by the crosslinks that are mutually inaccessible. We mean by this that, because of the possibility of interlocking closed loops formed by macromolecules, there will be families of configurations between which the system cannot continuously evolve without the necessity either of the breaking of at least one crosslink or the passage of one monomer through another. We distinguish between constraints arising indirectly from crosslinking via the interlocking of closed loops and constraints arising directly from the crosslinks themselves by referring to the former as *anholonomic* constraints and the latter as *holonomic* constraints. In principle, a statistical-mechanical approach should incorporate, at most, those configurations that are mutually accessible, i.e. should respect both holonomic and anholonomic constraints. The theory presented here treats the holonomic constraints as quenched but the anholonomic constraints as annealed, therefore not incorporating the latter. We know of no explicit semi-microscopic strategy that is capable of handling the anholonomic constraints.

2.3. Partition function

We define the statistical-mechanical partition function $\tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)$ that characterizes the crosslinked system via

$$\tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M) \equiv \left\langle \prod_{e=1}^M \delta^{(d)}(\mathbf{c}_{i_e}(s_e) - \mathbf{c}_{i'_e}(s'_e)) \right\rangle_1^E. \quad (2.8)$$

The product of Dirac δ -functions serves to remove from the sum over configurations implicit in the angle brackets (2.6) any configuration that fails to satisfy the constraints (2.7) [24], the remaining configurations contributing with weights given by the Edwards measure (2.5). With this definition, $\tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)$ is normalized relative to the uncrosslinked system. Consequently, the free energy derived from

this partition function will in fact be the increase in free energy that arises upon crosslinking. This allows us to focus on the implications of crosslinking rather than the properties of the uncrosslinked system.

At first sight, the quantity $\tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)$ in equation (2.8), which we are calling the partition function, appears to be precisely the physical partition function of the crosslinked system, at least relative to that of the uncrosslinked system. However, for a straightforward reason associated with the notion of indistinguishability, a reason that we discuss in sections 2.4 and 2.6, $\tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)$ as defined in equation (2.8) is not quite the correct definition of the physical partition function. However, as we shall see, the partition function $\tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)$ will turn out to be adequate for our purposes.

2.4. Indistinguishability

As first pointed out by Gibbs [23], the (configurational aspect of the) physical partition function for systems involving one or more species of identical constituents is to be found by summing over all configurations of the system whilst ignoring the issue of the distinguishability of the constituents, and subsequently dividing by an appropriate combinatorial factor to account for the indistinguishability of the constituents. This strategy compensates for the over-counting of configurations that has arisen from the neglect of indistinguishability.

What are the implications of indistinguishability in the present context? For the case of the system of N identical uncrosslinked macromolecules, the appropriate factor is $N!$, and thus the physical partition function is given by

$$\frac{1}{N!} \int \mathcal{D}\mathbf{c} \exp(-H_1^E). \quad (2.9)$$

If, for the case of the crosslinked system, the appropriate factor were also $N!$ (which it is not) then its physical partition function would be given by

$$\frac{1}{N!} \int \mathcal{D}\mathbf{c} \exp(-H_1^E) \prod_{e=1}^M \delta^{(d)}(\mathbf{c}_i(s_e) - \mathbf{c}_{i'}(s'_e)), \quad (2.10)$$

and thus the relative physical partition function would indeed be given by equation (2.8), the factors of $1/N!$ in the numerator and denominator cancelling.

However, the process of crosslinking alters the system from one that comprises N copies of a single species of identical elements. Instead, the crosslinked system will contain a variety of species, such as macromolecules that do not participate in any crosslinks, as well as clusters of macromolecules of many types. By clusters we mean assemblages of macromolecules that are (directly or indirectly) connected by crosslinks or interlockings, and therefore cannot be separated by arbitrary distances. Examples of clusters include pairs of macromolecules that participate in a single crosslink, that crosslink being located between some specific pair of arclength locations (say $(s, s') = (0.12, 0.57)$), single macromolecules crosslinked to themselves at some specific pair of arclength locations, triplets of macromolecules connected by two specifically located crosslinks, as well as more complicated species such as pairs of self-crosslinked macromolecules interlocking one another.

Let us label the various possible cluster species by the index $a = 1, 2, 3, \dots$, and let $a = 0$ label the uncrosslinked macromolecule species. Then, for a specific realization of the disorder (i.e. the crosslinks and the interlockings) let the number

of uncrosslinked macromolecules be ν_0 and the number of clusters of species a be ν_a [25]. Then the incorrect combinatorial factor of $N!$ should be replaced by the correct factor of $\prod_a \nu_a!$, this factor varying across disorder realizations. The physical partition function for a given realization of the system is then given by

$$\frac{1}{\prod_a \nu_a!} \int \mathcal{D}\mathbf{c} \exp(-H_1^E) \prod_{e=1}^M \delta^{(d)}(\mathbf{c}_{i_e}(s_e) - \mathbf{c}_{i'_e}(s'_e)). \quad (2.11)$$

This correction of the combinatorial factor is mirrored by the absence, due to the constraints, in the summation over system configurations of those configurations in which macromolecules participating in a cluster are widely separated, which results in the loss of volume factors. Together, the corrected combinatorial factor and the loss of volume factors conspire to yield a thermodynamic free energy that is properly extensive.

In common with much work on the physics of disordered systems, we shall not focus on the statistical mechanics of a system having a particular realization of the disorder. Instead we shall take a probabilistic approach, focusing on the typical properties of randomly crosslinked macromolecular systems. To do this, we shall need to consider the statistical distribution of crosslink locations. In fact, we shall also allow the number of crosslinks to fluctuate across realizations.

2.5. Deam–Edwards crosslink distribution

To compute physical quantities characterizing the system of randomly crosslinked macromolecules for a specific realization of the large set of quenched random variables $\{i_e, s_e; i'_e, s'_e\}_{e=1}^M$ is, of course, neither possible nor particularly useful. Instead we shall focus on *typical* values of physical quantities, constructed by suitably averaging them over the quenched random variables. To perform this averaging we shall need to choose a probability distribution that assigns a sensible statistical weight $\mathcal{P}_M(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)$ to each possible realization of the number M and location $\{i_e, s_e; i'_e, s'_e\}_{e=1}^M$ of the crosslinks. Following an elegant strategy due to Deam and Edwards [1], we assume that the normalized crosslink distribution is given by

$$\mathcal{P}_M(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M) = \frac{(\mu^2 V / 2N)^M \tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)}{M! \left\langle \exp \left\{ \frac{\mu^2 V}{2N} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \delta^{(d)}(\mathbf{c}_i(s) - \mathbf{c}_{i'}(s')) \right\} \right\rangle_1^E}, \quad (2.12)$$

where $\tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)$ is given by equation (2.8), and can be regarded as probing the equilibrium correlations of the underlying uncrosslinked liquid [26]. Such correlations were omitted from the crosslink distribution in certain previous works [8–11, 36], which led to difficulties in obtaining a quantitative description of the amorphous solid state. It is not, at present, clear whether this omission is significant for the liquid state.

The Deam–Edwards distribution can be envisaged as arising from a realistic vulcanization process, in which crosslinks are introduced simultaneously and instantaneously into the liquid state in equilibrium [27]. Specifically, it incorporates the notion that all pairs of monomers that happen (at some particular instant) to be nearby are, with a certain probability controlled by the crosslink density parameter μ^2 , crosslinked. Thus, the correlations of the crosslink distribution reflect the correlations of the uncrosslinked liquid, and it follows that realizations of crosslinks

only acquire an appreciable statistical weight if they are compatible with some reasonably probable configuration of the uncrosslinked liquid. This good feature of the Deam–Edwards distribution is compatible with the random, space-filling, *frozen liquid*, nature of the equilibrium amorphous state that is achieved upon sufficient crosslinking.

We allow the number of crosslinks to fluctuate in a quasi-Poisson manner, controlled by the parameter μ^2 . All that we shall need to know about μ^2 is that the mean number of crosslinks per macromolecule, which we denote by $[M]/N$, is a smooth, monotonically increasing function of μ^2 that can, in principle, be determined using the distribution \mathcal{P} [28]. We remark that the control parameter μ^2 appears in equation (2.12) divided by N/V . This factor is simply the (dimensionless) density of macromolecules, which is an intensive quantity. As we shall see, this choice leads to an equation of state that does not depend on the density of macromolecules, at least at the level of mean-field theory. We also remark that no delicate scaling of the control parameter is needed to achieve a good thermodynamic limit, in contrast with the case of the Sherrington–Kirkpatrick spin-glass model [30].

As discussed in section 2.2, at least in three dimensions crosslinking confers anholonomic topological constraints on the network as well as holonomic ones. Thus, the statistical-mechanical tool for constructing the crosslink distribution is not entirely correct. In principle, crosslink realizations should be labelled not only by $\{i_e, s_e; i'_e, s'_e\}_{e=1}^M$, i.e. by the number and arclength locations of the crosslinks, but also by the precise topology of the realization, i.e. by the manner in which the macromolecules thread through the closed loops made by one another. Then the statistical weight attributed to a crosslink-and-topology realization would be better modelled as arising from those configurations of the underlying equilibrium liquid that not only satisfy the holonomic constraints but also the anholonomic ones. As remarked in section 2.2, no mathematical tool yet exists for accomplishing this refinement analytically. In other words, we are treating the random topology of the system as annealed rather than quenched.

One should pause to notice the striking feature that at the heart of the Deam–Edwards crosslink distribution is the partition function $\tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)$ of the crosslinked system, i.e. the crosslink distribution is itself proportional to the partition function, the logarithm of which it is to be used to average. This fact gives the development a structure that is rather appealing, at least from the point of view of form. This will become especially apparent in section 4 in the context of the replica technique, in which this distribution is generated via an additional (i.e. zeroth) replica, the permutation aspect of the symmetry of the theory thereby being enlarged from the permutation group \mathcal{S}_n to \mathcal{S}_{n+1} , where n is the number of replicas [31, 32]. There is, however, no physical basis for restricting attention *solely* to crosslink distributions generated by the partition function identical to that of the crosslinked system. For example, one might imagine crosslinking at a different temperature or solvent quality, which would break the symmetry between the crosslink distribution and the partition function of the crosslinked system; then, in the context of the replica technique, the permutation aspect of the symmetry of the theory would remain \mathcal{S}_n .

2.6. Disorder averages and symmetry factors

How are we to use the Deam–Edwards crosslink distribution? As is well known, it is generally inappropriate in disordered systems to average the partition function

itself over the quenched random variables, as this would amount to treating the quenched random variables as annealed variables (i.e. equilibrated variables having the same status as the variables describing the configurations of the system that can be accessed during equilibrium fluctuations). Rather, it is thermodynamically extensive or intensive quantities, such as the free energy or the order parameter, that should be averaged over the quenched random variables [33]. To illustrate this point, consider the free energy relative to that of the uncrosslinked system, $-\ln \tilde{Z}$. (Recall that we are measuring energies in units such that $k_B T = 1$.) Then the disordered average of the free energy per macromolecule (relative to the free energy of the uncrosslinked system) per space dimension, which we denote \tilde{f} , is given by

$$-dN\tilde{f} = [\ln \tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)], \quad (2.13)$$

where the square brackets indicate a disorder average, viz

$$\begin{aligned} [\mathcal{O}_M(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)] &\equiv \mathcal{P}_0 \mathcal{O}_0 + \sum_{M=1}^{\infty} \int_0^1 ds_1 \cdots ds_M \int_0^1 ds'_1 \cdots ds'_M \\ &\times \sum_{i_1=1}^N \cdots \sum_{i_M=1}^N \sum_{i'_1=1}^N \cdots \sum_{i'_M=1}^N \mathcal{P}_M(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M) \mathcal{O}_M(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M), \end{aligned} \quad (2.14)$$

where $\mathcal{O}_M(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)$ is an arbitrary function of the realization of crosslinks. The average over the locations of the crosslinks excludes realizations of the disorder in which two positions on the same macromolecule located closer than a persistence length participate in crosslinks. This can be accomplished by suitably cutting off the arclength integrations. Inasmuch as \tilde{Z} is not strictly speaking the physical partition function, \tilde{f} is not strictly speaking the physical free energy. In fact, from equation (2.11) we know that the physical partition function (normalized with respect to that of the uncrosslinked system) is given by

$$Z(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M) = \frac{N!}{\prod_a \nu_a!} \tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M). \quad (2.15)$$

Thus, for the disorder-averaged physical free energy f , which is given by

$$-dNf \equiv [\ln Z(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)], \quad (2.16)$$

we obtain

$$-dNf = -dN\tilde{f} + \ln N! - \left[\ln \prod_a \nu_a! \right]. \quad (2.17)$$

Now, f is an intensive quantity. However, Δf , defined by

$$\Delta f \equiv f - \tilde{f} = -\frac{1}{dN} \left[\ln \left(\frac{\prod_a \nu_a!}{N!} \right) \right], \quad (2.18)$$

is in general proportional to $\ln N$ (for large N). The constant of proportionality is, in general, difficult to compute: it will, however, be a small number for the case of lightly crosslinked systems, increasing to d^{-1} in the high-crosslinking limit, for which all macromolecules are connected to a single cluster (for the uncrosslinked system $\Delta f = 0$). Thus \tilde{f} ($= f - \Delta f$) contains a term proportional to the logarithm of the size of the system, i.e. is not intensive. Despite this unphysical feature of \tilde{f} , it is \tilde{f} that we shall be computing, rather than f , because our inability to compute

[$\ln \prod_a \nu_a!$] precludes us from computing f . However, the physical properties of the system, such as the order parameter, for example, are determined by certain disorder-averaged quantities that we shall show to be insensitive to the indistinguishability factor $\prod_a \nu_a!$, and which can thus be computed in the present approach.

3. Order parameter for the amorphous solid state

3.1. General properties of the order parameter

We now discuss a certain order parameter constructed with the intention of distinguishing between equilibrium states that are liquid (in which the monomers are all delocalized), crystalline solid (in which a non-zero fraction are localized in a spatially periodic fashion), globular (in which the monomers have condensed within a spatial subvolume of the system), and amorphous solid (in which a non-zero fraction are localized in a spatially random fashion) [8–10]. This order parameter is an extension, *mutatis mutandis*, of the order parameter introduced by Edwards and Anderson in the context of a class of amorphous magnetic systems known as spin glasses [2, 33].

For a specific realization of the crosslinks (i.e. prior to disorder averaging), the appropriate order parameter is given by

$$\frac{1}{N} \sum_{i=1}^N \int_0^1 ds \langle \exp(i\mathbf{k}^1 \cdot \mathbf{c}_i(s)) \rangle_\chi \langle \exp(i\mathbf{k}^2 \cdot \mathbf{c}_i(s)) \rangle_\chi \cdots \langle \exp(i\mathbf{k}^g \cdot \mathbf{c}_i(s)) \rangle_\chi, \quad (3.1)$$

for $g = 1, 2, 3, \dots$, none of the d -dimensional wave vectors $\{\mathbf{k}^1, \dots, \mathbf{k}^g\}$ being zero. The angle brackets $\langle \cdots \rangle_\chi$ indicate an average over the equilibrium state in question for a particular realization of the disorder, indicated by the subscript χ . Such equilibrium states may correspond to situations in which the translational symmetry of the system is spontaneously broken, in which case they are not ergodic. However, we shall not dwell here on the possibility of further ergodicity breaking (e.g. of the type commonly associated with the concept of replica-symmetry breaking; see [33]). This restriction is consistent with the results presented below. For a discussion of ergodicity breaking in systems of crosslinked macromolecular networks, see [8–11, 31].

The disorder-averaged order parameter is denoted by

$$\left[\frac{1}{N} \sum_{i=1}^N \int_0^1 ds \langle \exp(i\mathbf{k}^1 \cdot \mathbf{c}_i(s)) \rangle_\chi \langle \exp(i\mathbf{k}^2 \cdot \mathbf{c}_i(s)) \rangle_\chi \cdots \langle \exp(i\mathbf{k}^g \cdot \mathbf{c}_i(s)) \rangle_\chi \right]. \quad (3.2)$$

For any particular positive integer g , this order parameter may be regarded as the g th moment of the distribution of random static density fluctuations $\mathcal{N}(\{\rho_{\mathbf{k}}\})$ (see [34]), which is defined by

$$\mathcal{N}(\{\rho_{\mathbf{k}}\}) \equiv \left[\frac{1}{N} \sum_{i=1}^N \int_0^1 ds \prod_{\mathbf{k}}^\dagger \delta_c(\rho_{\mathbf{k}} - \langle \exp(i\mathbf{k} \cdot \mathbf{c}_i(s)) \rangle_\chi) \right], \quad (3.3)$$

where $\prod_{\mathbf{k}}^\dagger$ denotes the product over all d -vectors \mathbf{k} in the half-space given by the condition $\mathbf{k} \cdot \mathbf{n} > 0$ for a suitable unit d -vector \mathbf{n} , and the Dirac δ -function of complex argument $\delta_c(z)$ is defined by $\delta_c(z) \equiv \delta(\text{Re } z) \delta(\text{Im } z)$, where $\text{Re } z$ and $\text{Im } z$ respectively denote the real and imaginary parts of the complex number z .

Thus,

$$\int \prod_{\mathbf{k}}^{\dagger} d(\operatorname{Re} \rho_{\mathbf{k}}) d(\operatorname{Im} \rho_{\mathbf{k}}) \mathcal{N}(\{\rho_{\mathbf{k}}\}) \rho_{\mathbf{k}^1} \rho_{\mathbf{k}^2} \cdots \rho_{\mathbf{k}^g}$$

$$= \left[\frac{1}{N} \sum_{i=1}^N \int_0^1 ds \langle \exp(i\mathbf{k}^1 \cdot \mathbf{c}_i(s)) \rangle_{\chi} \langle \exp(i\mathbf{k}^2 \cdot \mathbf{c}_i(s)) \rangle_{\chi} \cdots \langle \exp(i\mathbf{k}^g \cdot \mathbf{c}_i(s)) \rangle_{\chi} \right]. \quad (3.4)$$

To see why formula (3.1) is indeed an order parameter appropriate for distinguishing between liquid, crystalline, globular and amorphous solid states, let us examine its qualitative properties. First, suppose that the state is liquid. Then each monomer (i, s) is to be found, with equal probability, in the vicinity of any location in the container. Consequently, the equilibrium expectation value of its density $\langle \delta^{(d)}[\mathbf{r} - \mathbf{c}_i(s)] \rangle_{\chi}$ is the constant V^{-1} , and the Fourier transform $\langle \exp[i\mathbf{k} \cdot \mathbf{c}_i(s)] \rangle_{\chi}$ vanishes (except for the trivial case of $\mathbf{k} = \mathbf{0}$). Thus, for a liquid state the order parameter (3.1) vanishes, all terms in the summation over monomers vanishing identically. This corresponds to a state having full translational and rotational symmetry.

Next, consider the case when a non-zero fraction of monomers are localized in the vicinity of specific points in space, albeit exhibiting thermal fluctuations about these points. In this case, for many monomers (i, s) the quantity $\langle \delta^{(d)}[\mathbf{r} - \mathbf{c}_i(s)] \rangle_{\chi}$ will be more or less sharply peaked at some point in space and, correspondingly, $\langle \exp[i\mathbf{k} \cdot \mathbf{c}_i(s)] \rangle_{\chi}$ will not vanish identically, instead varying with \mathbf{k} so as to reflect the spatial localization of monomer (i, s). Then

$$\langle \exp(i\mathbf{k} \cdot \mathbf{c}_i(s)) \rangle_{\chi} = \exp(i\mathbf{k} \cdot \mathbf{b}_i(s)) \wp_{(i,s)}(\mathbf{k}), \quad (3.5)$$

where $\mathbf{b}_i(s)$ is the site about which monomer (i, s) is localized, and $\wp_{(i,s)}(\mathbf{k})$, which does not vanish identically, is the Fourier transform of the density of a monomer localized at the origin. In such a state, translational invariance is broken at the microscopic level. However, the symmetry of the state of the system at the microscopic level is not settled without further information.

What possibilities present themselves in the situation in which a non-zero fraction of the monomers are localized? If the mean locations $\{\mathbf{b}_i(s)\}$ of the localized monomers are distributed randomly and homogeneously over the volume of the system then the state is said to be macroscopically translationally invariant (MTI), the inclusion of rotational invariance being understood. We mean by this that there is no periodicity, or any other macroscopic feature capable of distinguishing one equilibrium state from any global translation or rotation of it. We refer to such states as (equilibrium) amorphous solid states. On the other hand, if the mean locations $\{\mathbf{b}_i(s)\}$ of the localized monomers are distributed inhomogeneously over the volume of the system then the state is said to break translational invariance macroscopically. Examples of such states are the globular state [35], in which the monomers have condensed (in space) within a subvolume of the system, and the crystalline state, in which the mean locations of the monomers are arranged in a periodic lattice (and the monomers may be regarded as having condensed in wave vector space).

How are the various possible states diagnosed by the order parameter? As we showed above, the order parameter is zero for all $\{\mathbf{k}^1, \dots, \mathbf{k}^g\}$ in a state that is translationally invariant at the microscopic level (i.e. a liquid). On the other hand, it will take at least some non-zero values for any state in which translational invariance

is broken at the microscopic level. By using equation (3.5) we see that in such a state the order parameter (3.1) becomes

$$\frac{1}{N} \sum_{i=1}^N \int_0^1 ds \varphi_{(i,s)}(\mathbf{k}^1) \varphi_{(i,s)}(\mathbf{k}^2) \cdots \varphi_{(i,s)}(\mathbf{k}^g) \exp(i(\mathbf{k}^1 + \mathbf{k}^2 + \cdots + \mathbf{k}^g) \cdot \mathbf{b}_i(s)). \quad (3.6)$$

This order parameter also provides a way to distinguish between non-liquid states that are MTI and those that are not. In the case of an MTI state the summation of complex phase factors will totally destructively interfere unless the wave vectors happen to sum to zero, the random locations of the mean monomer positions otherwise leading to random phase cancellations. Hence, the order parameter will only fail to vanish for values of the wave vectors $\{\mathbf{k}^1, \mathbf{k}^2, \dots, \mathbf{k}^g\}$ that sum to zero. This property of being MTI is a fundamental characteristic of the amorphous solid state. In the non-MTI case total destructive interference is avoided not only if the wave vectors sum to zero but also under other circumstances. Hence, in this case the order parameter will also fail to vanish for certain values of the wave vectors $\{\mathbf{k}^1, \mathbf{k}^2, \dots, \mathbf{k}^g\}$ that do not sum to zero. To establish this, consider how formula (3.6) transforms under a global translation by an arbitrary vector \mathbf{a} :

$$\begin{aligned} & \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \varphi_{(i,s)}(\mathbf{k}^1) \varphi_{(i,s)}(\mathbf{k}^2) \cdots \varphi_{(i,s)}(\mathbf{k}^g) \exp(i(\mathbf{k}^1 + \mathbf{k}^2 + \cdots + \mathbf{k}^g) \cdot \mathbf{b}_i(s)) \\ & \rightarrow \exp(i(\mathbf{k}^1 + \mathbf{k}^2 + \cdots + \mathbf{k}^g) \cdot \mathbf{a}) \\ & \quad \times \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \varphi_{(i,s)}(\mathbf{k}^1) \varphi_{(i,s)}(\mathbf{k}^2) \cdots \varphi_{(i,s)}(\mathbf{k}^g) \exp(i(\mathbf{k}^1 + \mathbf{k}^2 + \cdots + \mathbf{k}^g) \cdot \mathbf{b}_i(s)). \end{aligned} \quad (3.7)$$

In situations of MTI, this transformation must leave the order parameter unchanged for all vectors \mathbf{a} . This enforces the condition that for MTI situations the order parameter must vanish unless $\mathbf{k}^1 + \mathbf{k}^2 + \cdots + \mathbf{k}^g = \mathbf{0}$, and thus the order parameter becomes

$$\delta_{\mathbf{0}, \mathbf{k}^1 + \cdots + \mathbf{k}^g} \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \varphi_{(i,s)}(\mathbf{k}^1) \cdots \varphi_{(i,s)}(\mathbf{k}^g), \quad (3.8)$$

where $\delta_{\mathbf{p}^1, \mathbf{p}^2}$ is a d -dimensional Kronecker δ -factor, which is non-zero only if the d -vectors \mathbf{p}^1 and \mathbf{p}^2 have all components equal, in which case it has the value unity. In this state, in contrast with the crystalline state, there is no periodicity associated with the spatial pattern of localized monomers, and thus there will not be a collection of reciprocal lattice vectors for which the order parameter fails to vanish. In particular, the order parameter vanishes for $g = 1$. (One may equivalently regard the amorphous solid state as the special case of the crystalline state in which the unit cell of the crystal is the entire sample, i.e. a realization of Schrödinger's 'aperiodic solid' [36].) The equilibrium amorphous solid state is characterized by the presence of random (i.e. non-periodic) static density fluctuations, which spontaneously break translational symmetry at the microscopic (but not the macroscopic) level.

In the non-MTI case, either the transformation (3.7) must leave the order parameter unchanged for a discrete lattice of vectors \mathbf{a} , or it need not leave the order parameter unchanged for any value of \mathbf{a} . When there is invariance for a discrete lattice of vectors (i.e. in the crystalline state), the order parameter must

vanish unless $\mathbf{k}^1 + \mathbf{k}^2 + \dots + \mathbf{k}^g = \mathbf{G}$, where \mathbf{G} is any reciprocal lattice vector of the crystal (including the zero reciprocal lattice vector). When there is no vector for which the invariance holds (i.e. in the globular state) the order parameter need not vanish on symmetry grounds for any values of the wave vectors $\{\mathbf{k}^1, \dots, \mathbf{k}^g\}$.

To summarize, the values of the order parameter for the various values of g and the wave vectors $\{\mathbf{k}^1, \mathbf{k}^2, \dots, \mathbf{k}^g\}$ serve to distinguish between liquid, crystalline, globular and amorphous solid states: for liquid states the order parameter vanishes for $g = 1, 2, 3, \dots$; for amorphous solid states it vanishes for all wave vectors that do not sum to zero (and thus vanishes for $g = 1$); for crystalline states it only vanishes for wave vectors that fail to sum to a reciprocal lattice vector (and therefore is non-zero for some $\{\mathbf{k}^1, \mathbf{k}^2, \dots, \mathbf{k}^g\}$, even when $g = 1$); and for globular states it need not vanish on symmetry grounds for any values of $\{\mathbf{k}^1, \mathbf{k}^2, \dots, \mathbf{k}^g\}$.

3.2. A simple idealization: generalized Einstein model

To illustrate the general properties of the order parameter, and to motivate the specific hypothesis for the form of the order parameter described in section 3.3 and applied in section 6, we examine a simple caricature of the amorphous solid state. We refer to this caricature as a generalized Einstein model, by analogy with the Einstein model of a crystalline solid adopted for the computation of the specific heat, in which it is assumed that every atom is independently localized by an identical harmonic potential [37]. In the context of amorphous solidification, the caricature is obtained by asserting that a fraction $(1 - q)$ of the monomers (the so-called sol fraction) are delocalized, with each monomer (i, s) of the remaining fraction q (the so-called gel fraction) being localized near a random mean position $\mathbf{b}_i(s)$, its location exhibiting thermal fluctuations about that mean position. We emphasize that our usage of the terms gel and sol in this article refers solely to the issue of whether or not a monomer is localized. Ultimately, however, we shall see that the gel fraction defined in this way coincides with the more common architectural definition, in the sense that localization will be seen to occur only for crosslink densities for which the network spans the entire system. It is further asserted that the probability distribution for the fluctuations in location of each localized monomer (i, s) about its mean position is Gaussian and isotropic, and characterized by an inverse square localization length $\tau_i(s)$. Then, if (i, s) is a localized monomer, its Fourier-transformed density would be given by

$$\langle \exp(i\mathbf{k} \cdot \mathbf{c}_i(s)) \rangle_\chi = \exp(i\mathbf{k} \cdot \mathbf{b}_i(s)) \exp(-k^2/2\tau_i(s)), \quad (3.9)$$

so that the order parameter (prior to disorder-averaging) becomes

$$(1 - q) \prod_{a=1}^g \delta_{\mathbf{0}, \mathbf{k}^a} + \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp\left(i\mathbf{b}_i(s) \cdot \sum_{a=1}^g \mathbf{k}^a\right) \exp\left(-\sum_{a=1}^g |\mathbf{k}^a|^2/2\tau_i(s)\right), \quad (3.10)$$

where it is understood that the summation in the second term only includes localized monomers.

To obtain the disorder-average of the order parameter we assume that for each monomer (i, s) the random variables $\mathbf{b}_i(s)$ and $\tau_i(s)$ are uncorrelated. Furthermore we assume that $\mathbf{b}_i(s)$ is uniformly distributed over the volume V and that the inverse square localization length $\tau_i(s)$ has the probability distribution $p(t)$. (The notion that the state could be characterized by a statistical distribution of localization lengths

was introduced in [10] and implemented in [13].) In this case the order parameter becomes

$$(1 - q) \prod_{a=1}^g \delta_{0, \mathbf{k}^a}^{(d)} + q \delta_{0, \sum_{a=1}^g \mathbf{k}^a}^{(d)} \int_0^\infty d\tau p(\tau) \exp\left(-\sum_{a=1}^g |\mathbf{k}^a|^2 / 2\tau\right). \quad (3.11)$$

The first term accounts for the delocalized monomers, and the second term accounts for the localized monomers. If $q = 0$ then the state described by this order parameter is the liquid state. If $q \neq 0$ then it describes an amorphous solid state. The Kronecker δ factor in front of the second term is a reflection of the MTI that characterizes the amorphous solid state. This hypothesis is a refinement of the Gaussian hypothesis used in a number of contexts [38]. It is useful to observe that the gel fraction q can be extracted from the order parameter (3.1) by taking the limit of the order parameter as $\{\mathbf{k}^1, \dots, \mathbf{k}^g\} \rightarrow \{0, \dots, 0\}$ through a sequence for which $\sum_{a=1}^g \mathbf{k}^a = 0$.

3.3. Replica-order-parameter hypothesis: gel fraction and distribution of localization lengths

Having discussed the physical order parameter capable of diagnosing equilibrium amorphous solidification, we now anticipate the development of the replica approach by describing the particular form that we shall hypothesize for the replica order parameter, i.e. the order parameter that emerges from the application of the replica technique and represents, in the replica approach, the physical order parameter discussed in the previous two subsections of the present section. This form is motivated by the general characterization of amorphous solidification in terms of the gel fraction q and the distribution of inverse square localization lengths $p(\tau)$ given in section 3.2. Below, in section 6, we shall show that within the context of a certain model of randomly crosslinked macromolecular networks the form that we now hypothesize for the replica order parameter is sufficiently broad to allow us to provide an exact and physically appealing mean-field-level description of the transition to and properties of the equilibrium amorphous solid state of randomly crosslinked macromolecular networks.

As we shall see in detail in section 4, the replica representation of the physical order parameter is given by

$$\left\langle \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp\left(i \sum_{\alpha=0}^n \mathbf{k}^\alpha \cdot \mathbf{c}_i^\alpha(s)\right) \right\rangle_{n+1}^P, \quad (3.12)$$

in the replica limit, $n \rightarrow 0$. As we shall also see there, $\langle \dots \rangle_{n+1}^P$ denotes an expectation value for a pure (i.e. quenched-disorder-free) system of $n + 1$ coupled replicas of the original macromolecular system. Note the inclusion of degree of freedom associated with a replica labelled by $\alpha = 0$. For the sake of notational convenience we introduce hatted vectors (e.g. \hat{k} or \hat{c}), which are $(n + 1)d$ -component vectors comprising $(n + 1)$ -fold replicated sets of d -component vectors (e.g. the wave vectors $\{\mathbf{k}^0, \mathbf{k}^1, \dots, \mathbf{k}^n\}$ or the position vectors $\{\mathbf{c}^0, \mathbf{c}^1, \dots, \mathbf{c}^n\}$). We define the extended scalar product $\hat{k} \cdot \hat{c}$ by $\hat{k} \cdot \hat{c} \equiv \sum_{\alpha=0}^n \mathbf{k}^\alpha \cdot \mathbf{c}^\alpha$, having the special cases $\hat{k}^2 \equiv \hat{k} \cdot \hat{k}$ and $\hat{c}^2 \equiv \hat{c} \cdot \hat{c}$. In terms of this notation, the order parameter becomes

$$\left\langle \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}_i(s)) \right\rangle_{n+1}^P. \quad (3.13)$$

By translating formula (3.11) into the replica language, through the use of equation (4.19), we are led to the assumption that the replica order parameter takes on values expressible in the form

$$(1 - q) \delta_{\hat{k}, \hat{0}}^{(nd+d)} + q \delta_{\mathbf{k}, \mathbf{0}}^{(d)} \int_0^\infty d\tau p(\tau) \exp(-\hat{k}^2/2\tau), \quad (3.14)$$

where $\hat{\mathbf{k}} \equiv \sum_{\alpha=0}^n \mathbf{k}^\alpha$ is a permutation-invariant d -vector built by summing the elements of the replicated vector $\hat{\mathbf{k}}$, and $\delta_{\hat{k}, \hat{0}}^{(nd+d)} \equiv \prod_{\alpha=0}^n \delta_{\mathbf{k}^\alpha, \mathbf{0}}$. Thus, we parametrize the order parameter in terms of the gel fraction q and the distribution of (inverse square) localization lengths $p(\tau)$ [39]. This parametrization is severely restrictive but physically plausible. In order for $p(\tau)$ to be interpreted as a probability distribution it must be non-negative. This condition is not imposed *a priori*, but emerges from the stationarity condition. The ranging of τ only over positive values reflects the fact that inverse square localization lengths are positive. Moreover, delocalized monomers are accounted for by the term proportional to $(1 - q)$, so that $p(\tau)$ must not contain a Dirac δ -function-like piece at $\tau = 0$. The factor $\delta_{\mathbf{k}, \mathbf{0}}^{(d)}$ incorporates the MTI property into the hypothesized form. It should be emphasized that the hypothesized form is invariant under the permutation of the replicated vectors $\{\mathbf{k}^0, \mathbf{k}^1, \dots, \mathbf{k}^n\}$, which is a manifestation of its replica-symmetric character.

3.4. Symmetry properties of the order parameter hypothesis

We now state explicitly the symmetry properties of the order parameter hypothesis (3.14) that we shall use throughout the remainder of this article. As we shall see in section 4, the effective Hamiltonian of the replica theory turns out to have the following symmetries: (i) independent translations or rotation of the replicas, and (ii) permutations of the replicas. In the liquid state the order parameter retains all these symmetries. In the amorphous solid state the symmetry of the order parameter is reduced. By invoking our hypothesis for the order parameter we are assuming that in the amorphous solid state the residual symmetries are: (i') common translations and rotations of the replicas, and (ii) permutations of the replicas. In other words, in the transition to the amorphous solid state the symmetry of independent translations and rotations of the replicas is spontaneously broken. As a consequence of the spontaneous breaking of certain symmetries there is a manifold of symmetry-related values of the order parameter that describe the solid state.

In this article we have restricted our attention to order-parameter hypotheses that are invariant under the permutations of all $(n + 1)$ replicas (i.e. that are replica symmetric). This mathematical restriction is equivalent to the physical condition that, upon amorphous solidification, the (overwhelming fraction of the) system must exhibit one member of a unique family of equilibrium states (i.e. statistical arrangements of the macromolecules), this unique family of states being related by global translations and rotations. Whilst the occurrence of a unique family would not be an unreasonable consequence of crosslinking, especially in view of our exclusion of the anholonomic constraints that crosslinking introduces into the physical system, one might anticipate that crosslinking would cause the full physical system to exhibit many families of states (i.e. there would be states that are not related by global translations and rotations). Such an occurrence would be signalled by an order parameter that is no longer invariant under permutations of the replicas (i.e. for which replica symmetry is spontaneously broken). For discussions of these matters, see [31] as well as [8–11]. The issue of whether or not there exists a more

accurate treatment of randomly crosslinked macromolecular systems that would indicate the existence of many unsymmetry-related states is a matter of ongoing research [41].

It must, however, be emphasized that, regardless of the issue of the intactness of permutation symmetry, the primary physical phenomenon at hand in the formation of the equilibrium amorphous solid state is the spontaneous breaking of translation symmetry (viz the spontaneous random localization of macromolecules). The issue of replica-symmetry-breaking is not an alternative to translational-symmetry-breaking: it simply addresses whether or not a system with given realization of crosslinking possesses one or many unsymmetry-related ways for the macromolecules to be randomly localized. To allow for the possibility that replica-symmetry-breaking accompanies translational-symmetry-breaking is to explore a more general class of behaviours of the system.

3.5. Connection with scattering experiments

The order parameter that we have been addressing in the present section is, in principle, accessible via neutron scattering experiments [42, 43], at least for the case $g = 2$. In fact, the elastic part of the differential scattering cross-section (per atom) can be written as

$$\frac{1}{N} \frac{d^2\sigma}{d\Omega} = S^{\text{el}}(\mathbf{q}) = \lim_{t \rightarrow \infty} \left(\frac{|b_{\text{coh}}|^2}{N} \left\langle \sum_{i,i'=1}^N \int_0^1 ds ds' \exp(-i\mathbf{q} \cdot \mathbf{c}_i(s;0)) \exp(i\mathbf{q} \cdot \mathbf{c}_{i'}(s';t)) \right\rangle + \frac{|b_{\text{incoh}}|^2}{N} \left\langle \sum_{i=1}^N \int_0^1 ds \exp(-i\mathbf{q} \cdot \mathbf{c}_i(s;0)) \exp(i\mathbf{q} \cdot \mathbf{c}_i(s;t)) \right\rangle \right), \quad (3.15)$$

where b_{coh} is the average scattering length, b_{incoh} is the variance of the scattering length, $\mathbf{c}_i(s;t)$ is the position of monomer s on macromolecule i at time t , and $\langle \dots \rangle$ indicates a time-dependent equilibrium expectation value. The second part on the right hand side is the *incoherent* contribution, and can be extracted in some cases. By using the fact that the connected correlators vanish for $t \rightarrow \infty$, we see that this second part reduces to

$$\frac{|b_{\text{incoh}}|^2}{N} \sum_{i=1}^N \int_0^1 ds \langle \exp(-i\mathbf{q} \cdot \mathbf{c}_i(s)) \rangle \langle \exp(i\mathbf{q} \cdot \mathbf{c}_i(s)) \rangle, \quad (3.16)$$

i.e. formula (3.1) evaluated for the special case of $\{\mathbf{k}^1, \mathbf{k}^2, \dots, \mathbf{k}^g\} = \{-\mathbf{q}, \mathbf{q}, \mathbf{0}, \dots, \mathbf{0}\}$. Thus, the order parameter for $g = 2$ is proportional to the incoherent part of the elastic neutron scattering cross-section.

Oeser *et al.* [44] have measured the time persistent part of the incoherent scattering function in neutron-spin-echo experiments. They fit their data, which are taken in the high crosslinking limit, to a Gaussian in wave vector space characterized by a typical length scale l , which turns out to be comparable to the radius of gyration. A potential critique of neutron scattering experiments results from the available time scales, of order 10 ns, which make it difficult to extrapolate to infinite time in order to extract the time-persistent part of the autocorrelation. This may not be a severe problem in the high crosslinking limit, in which one expects rather small time scales associated with small distances between crosslinks. However, it may become prohibitive for weakly crosslinked systems, which barely sustain an infinite cluster.

Pulsed field gradient NMR (see, for example, [45]) is another experimental technique for measuring the intermediate-time incoherent scattering function with

a spatial and temporal resolution that is complementary to neutron scattering experiments. Typical time scales in NMR experiments are of the order of milliseconds, and length scales are restricted to be greater than 10 nm. An example of such measurements is the detection of spatial fluctuations in swollen networks in [46].

4. Replica approach for disorder-averaged quantities

Having prepared the way by discussing the model and the construction of a suitable probability distribution for the disorder, and defining an order parameter capable of diagnosing the possible states of the system, we now turn to the computation of disorder averages of important physical quantities, such as the free energy, order parameter and certain correlators. A direct assault on this task, as it stands, seems prohibitively difficult, but it can be rendered tractable by the use of the replica technique [33], pioneered in the context of macromolecular networks by Deam and Edwards [1]. In this approach, we do not consider just the original degrees of freedom but, instead, a system comprising $n + 1$ interacting copies (i.e. replicas) of it that will be labelled by the superscript $\alpha = 0, 1, \dots, n$. In this new system, the quenched randomness disappears from the formulation, at the price of introducing an inter-replica interaction.

4.1. Replica-Helmholtz free energy

In order to compute quantities such as the disorder-averaged free energy, the order parameter and the elastic free energy [47] in a unified way, it is particularly convenient to introduce a certain generating functional $\Phi_n(\mu^2, \{U\})$, which we refer to as the replica-Helmholtz free energy and define as follows:

$$\begin{aligned} \exp(-ndN\Phi_n(\mu^2, \{U\})) \equiv & \frac{\left\langle \exp \left\{ -\frac{\lambda^2}{2} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \sum_{\alpha=0}^n \delta^{(d)}(\mathbf{c}_i^\alpha(s) - \mathbf{c}_{i'}^\alpha(s')) \right\} \right. \\ & \times \exp \left\{ \frac{\mu^2 V}{2N} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \prod_{\alpha=0}^n \delta^{(d)}(\mathbf{c}_i^\alpha(s) - \mathbf{c}_{i'}^\alpha(s')) \right\} \\ & \left. \times \exp \left\{ -\frac{V^{n+1}}{N} \sum_{i=1}^N \int_0^1 ds U(\hat{\mathbf{c}}_i(s)) \right\} \right\rangle_{n+1}^W}{\left\langle \exp \left\{ -\frac{\lambda^2}{2} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \delta^{(d)}(\mathbf{c}_i(s) - \mathbf{c}_{i'}(s')) \right\} \right. \\ & \left. \times \exp \left\{ \frac{\mu^2 V}{2N} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \delta^{(d)}(\mathbf{c}_i(s) - \mathbf{c}_{i'}(s')) \right\} \right\rangle_1^W} \quad (4.1) \end{aligned}$$

The expectation value $\langle \dots \rangle_{n+1}^W$ is defined to be

$$\langle \dots \rangle_{n+1}^W \equiv \frac{\int \prod_{\alpha=0}^n \mathcal{D}\mathbf{c}^\alpha \exp(-H_{n+1}^W) \dots}{\int \prod_{\alpha=0}^n \mathcal{D}\mathbf{c}^\alpha \exp(-H_{n+1}^W)}, \quad (4.2)$$

i.e. an average with respect to the $(n + 1)$ -fold replicated Wiener measure, which is proportional to $\exp(-H_{n+1}^W)$, where

$$H_{n+1}^W = \frac{1}{2} \sum_{\alpha=0}^n \sum_{i=1}^N \int_0^1 ds \left| \frac{d}{ds} \mathbf{c}_i^\alpha(s) \right|^2. \quad (4.3)$$

In analogy with magnetic systems, the properties of which one can probe by computing the free energy as a function of an external, position-dependent, magnetic field, it is useful in the present context to introduce the external potential U on which Φ_n depends. The potential U , which takes as its argument an $(n+1)$ -fold replicated d -vector \hat{x} , acts simultaneously on replicas of all monomers, has zero average (over \hat{x}), and plays the role of a source field. As we shall now show, knowledge of $\Phi_n(\mu^2, \{U\})|_{U=0}$ allows us to compute the disorder-averaged free energy per macromolecule $d\bar{f}$. Subsequently, we shall see that by (functional) differentiation of $\Phi_n(\mu^2, \{U\})$ with respect to U we shall be able to compute the order parameter. Furthermore, it is possible to investigate the elastic properties of the amorphous solid state of randomly crosslinked macromolecular networks by making a Legendre transformation with respect to U (see [47]).

The quantity $Q_{\hat{k}}$, defined by

$$Q_{\hat{k}} \equiv \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}_i(s)), \quad (4.4)$$

is the Fourier transform of the replicated monomer density. As we shall see in section 4.3, a certain average of $Q_{\hat{k}}$ turns out to be the replica representation of the order parameter. In order to generate $Q_{\hat{k}}$ it is useful to introduce the Fourier representation of the external potential U , viz

$$U(\hat{c}) = \frac{1}{V^{n+1}} \sum_{\hat{k}} U_{\hat{k}} \exp(i\hat{k} \cdot \hat{c}), \quad (4.5)$$

which leads to the replacement

$$\frac{V^{n+1}}{N} \sum_{i=1}^N \int_0^1 ds U(\hat{c}_i(s)) \rightarrow \sum_{\hat{k}} U_{\hat{k}} Q_{\hat{k}} \quad (4.6)$$

in equation (4.1), so that $U_{\hat{k}}$ is a source for $Q_{\hat{k}}$. We shall, in addition, make use of expectation values involving the weight that features in the replica-Helmholtz free energy, equation (4.1):

$$\begin{aligned} & \left\langle \cdots \exp \left\{ -\frac{\lambda^2}{2} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \sum_{\alpha=0}^n \delta^{(d)}(\mathbf{c}_i^\alpha(s) - \mathbf{c}_{i'}^\alpha(s')) \right\} \right. \\ & \quad \times \exp \left\{ \frac{\mu^2 V}{2N} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \prod_{\alpha=0}^n \delta^{(d)}(\mathbf{c}_i^\alpha(s) - \mathbf{c}_{i'}^\alpha(s')) \right\} \\ & \quad \left. \times \exp \left(-\sum_{\hat{k}} U_{\hat{k}} Q_{\hat{k}} \right) \right\rangle_{n+1}^W \\ \langle \cdots \rangle_{n+1,U}^P & \equiv \frac{\left\langle \cdots \exp \left\{ -\frac{\lambda^2}{2} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \sum_{\alpha=0}^n \delta^{(d)}(\mathbf{c}_i^\alpha(s) - \mathbf{c}_{i'}^\alpha(s')) \right\} \right.}{\left\langle \exp \left\{ -\frac{\lambda^2}{2} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \sum_{\alpha=0}^n \delta^{(d)}(\mathbf{c}_i^\alpha(s) - \mathbf{c}_{i'}^\alpha(s')) \right\} \right.} \\ & \quad \times \exp \left\{ \frac{\mu^2 V}{2N} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \prod_{\alpha=0}^n \delta^{(d)}(\mathbf{c}_i^\alpha(s) - \mathbf{c}_{i'}^\alpha(s')) \right\} \\ & \quad \left. \times \exp \left(-\sum_{\hat{k}} U_{\hat{k}} Q_{\hat{k}} \right) \right\rangle_{n+1}^W \quad (4.7) \end{aligned}$$

The superscript P indicates that the average is taken over a pure system; the subscript $n + 1$ indicates that the system comprises $n + 1$ coupled replicas. In fact we shall also find ourselves making use of the zero-potential expectation value $\langle \dots \rangle_{n+1, U=0}^P$, for which we introduce the special notation $\langle \dots \rangle_{n+1}^P$.

The definitions given in the present subsection give the basic mathematical objects that we shall manipulate in our formulation. As was anticipated above, the quenched randomness associated with the random crosslinks does not appear explicitly in these definitions, but instead a term proportional to μ^2 appears, which introduces a coupling between the replicas. In contrast with the case of conventional spin glass models [33], the replica interaction couples all the replicas simultaneously, rather than pairwise. This feature is responsible for the occurrence of an order parameter involving a product over all the replicas, rather than pairs of replicas. For a similar feature in the context of dilute spin glasses, see [48].

4.2. Application of the replica-Helmholtz free energy to the free energy \bar{f}

We now show how knowledge of $\Phi_n(\mu^2, \{0\})$ allows us to obtain the disorder-averaged free energy per macromolecule $d\bar{f}$, defined in equation (2.13). To see this, consider the quotient

$$\exp(-ndN\Phi_n(\mu^2, \{0\}))/\exp(-ndN\Phi_n(0, \{0\})). \quad (4.8)$$

By using equation (4.1) we see that this quotient is given by

$$\frac{\exp(-ndN\Phi_n(\mu^2, \{0\}))}{\exp(-ndN\Phi_n(0, \{0\}))} = \frac{\left\langle \exp \left\{ \frac{\mu^2 V}{2N} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \prod_{\alpha=0}^n \delta^{(d)}(\mathbf{c}_i^\alpha(s) - \mathbf{c}_{i'}^\alpha(s')) \right\} \right\rangle_{n+1}^E}{\left\langle \exp \left\{ \frac{\mu^2 V}{2N} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \delta^{(d)}(\mathbf{c}_i(s) - \mathbf{c}_{i'}(s')) \right\} \right\rangle_1^E} \quad (4.9)$$

Here, we have transformed the expectation values from ones weighted by the replicated Wiener measure, equation (4.3), to ones weighted by the replicated Edwards measure, which is proportional to $\exp(-H_{n+1}^E)$, in which

$$H_{n+1}^E \equiv \frac{1}{2} \sum_{\alpha=0}^n \sum_{i=1}^N \int_0^1 ds \left| \frac{d}{ds} \mathbf{c}_i^\alpha(s) \right|^2 + \frac{\lambda^2}{2} \sum_{\alpha=0}^n \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \delta^{(d)}(\mathbf{c}_i^\alpha(s) - \mathbf{c}_{i'}^\alpha(s')). \quad (4.10)$$

We indicate such expectation values by $\langle \dots \rangle_{n+1}^E$, the subscript $n + 1$ indicating the presence of replicas. Next, we replace the exponential function in the numerator of equation (4.9) by its power series expansion, thus obtaining

$$\frac{\exp(-ndN\Phi_n(\mu^2, \{0\}))}{\exp(-ndN\Phi_n(0, \{0\}))} = \frac{\left\langle \sum_{M=0}^{\infty} \frac{1}{M!} \left(\frac{\mu^2 V}{2N} \right)^M \left\{ \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \prod_{\alpha=0}^n \delta^{(d)}(\mathbf{c}_i^\alpha(s) - \mathbf{c}_{i'}^\alpha(s')) \right\}^M \right\rangle_{n+1}^E}{\left\langle \exp \left\{ \frac{\mu^2 V}{2N} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \delta^{(d)}(\mathbf{c}_i(s) - \mathbf{c}_{i'}(s')) \right\} \right\rangle_1^E}. \quad (4.11)$$

By expressing the M th power as a multiple summation and integral over products we obtain

$$\frac{\exp(-ndN\Phi_n(\mu^2, \{0\}))}{\exp(-ndN\Phi_n(0, \{0\}))} = \frac{\left\langle \sum_{M=0}^{\infty} \frac{1}{M!} \left(\frac{\mu^2 V}{2N}\right)^M \sum_{i_1, i'_1=1}^N \cdots \sum_{i_M, i'_M=1}^N \int_0^1 ds_1 \int_0^1 ds'_1 \cdots \int_0^1 ds_M \int_0^1 ds'_M \prod_{\alpha=0}^n \prod_{e=1}^M \delta^{(d)}(\mathbf{c}_{i_e}^{\alpha}(s_e) - \mathbf{c}_{i'_e}^{\alpha}(s'_e)) \right\rangle_{n+1}^E}{\left\langle \exp\left\{\frac{\mu^2 V}{2N} \sum_{i, i'=1}^N \int_0^1 ds \int_0^1 ds' \delta^{(d)}(\mathbf{c}_i(s) - \mathbf{c}_{i'}(s'))\right\} \right\rangle_1^E}. \quad (4.12)$$

We now recognize that the expectation value in the numerator factorizes on the replica index to give $n+1$ factors of the partition function $\tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)$, equation (2.8). One of these factors, when taken together with the denominator and remaining terms (i.e. factors other than n partition functions), reconstructs the Deam–Edwards probability distribution, equation (2.12). Thus, by using equation (2.14) we obtain

$$\frac{\exp(-ndN\Phi_n(\mu^2, \{0\}))}{\exp(-ndN\Phi_n(0, \{0\}))} = \sum_{M=0}^{\infty} \sum_{i_1, i'_1=1}^N \cdots \sum_{i_M, i'_M=1}^N \int_0^1 ds_1 \int_0^1 ds'_1 \cdots \int_0^1 ds_M \int_0^1 ds'_M \times \mathcal{P}_M(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M) \tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)^n \quad (4.13 a)$$

$$= [\tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)]^n. \quad (4.13 b)$$

By taking the logarithm of both sides, and using the expansions

$$z^n = \exp(n \ln z) = 1 + n \ln z + \mathcal{O}(n^2), \quad (4.14 a)$$

$$\ln(1 + nz) = nz + \mathcal{O}(n^2), \quad (4.14 b)$$

valid for small n , we arrive at the relationship between the replica-Helmholtz free energy $\Phi_n(\mu^2, \{U\})$ and the disorder-averaged free energy per macromolecule $d\tilde{f}$ of equation (2.13):

$$\lim_{n \rightarrow 0} (\Phi_n(\mu^2, \{0\}) - \Phi_n(0, \{0\})) = \tilde{f}. \quad (4.15)$$

4.3. Application of the replica-Helmholtz free energy to disorder-averaged observables

In the previous subsection we discussed the application of the replica technique to the computation of the disorder-averaged free energy. We now turn to the issue of the computation of disorder averages of equilibrium expectation values of physical observables as well as of disorder averages of sums of products of equilibrium expectation values of physical observables. As we have seen in section 3, the latter type of quantity arises in the context of the order parameter for equilibrium amorphous solidification. This computation is accomplished by using the connection between the replica-Helmholtz free energy $\Phi_n(\mu^2, \{U\})$, equation (4.1), and expectation values of $Q_{\hat{k}}$, equation (4.4):

$$\frac{\delta}{\delta U_{\hat{k}}} ndN\Phi_n(\mu^2, \{U\}) = \langle Q_{\hat{k}} \rangle_{n+1, U}^P \quad (4.16)$$

More generally, by (functional) differentiation of $\Phi_n(\mu^2, \{U\})$ with respect to U we can obtain average values for powers of the order parameter, viz

$$ndN\Phi_n(\mu^2, \{U\}) = ndN\Phi_n(\mu^2, \{0\}) + \sum_{r=1}^{\infty} \frac{(-1)^{r+1}}{r!} \sum_{\hat{k}_1} \cdots \sum_{\hat{k}_r} U_{\hat{k}_1} \cdots U_{\hat{k}_r} \langle Q_{\hat{k}_1} \cdots Q_{\hat{k}_r} \rangle_{n+1,c}^P \quad (4.17)$$

The subscript c indicates that the correlators are connected ones [49, 50].

Now, equations (4.16) and (4.17) exhibit relationships between quantities defined in the framework of pure systems of replicated degrees of freedom. On the other hand, as discussed in section 3, the state of the system is appropriately diagnosed in terms of an order parameter built from the disorder average of products of expectation values taken in the (unreplicated) physical system. The connection between the former (replica) quantities and the later (non-replica) quantities is contained in the following formula, established in Appendix A, which is valid in replica-symmetric states [33]:

$$\langle [\mathcal{O}_0]_X \langle \mathcal{O}_1 \rangle_X \cdots \langle \mathcal{O}_g \rangle_X \rangle = \lim_{n \rightarrow 0} \langle \mathcal{O}_0(\{\mathbf{c}_i^0(s)\}) \cdots \mathcal{O}_g(\{\mathbf{c}_i^g(s)\}) \rangle_{n+1}^P \quad (4.18)$$

The most important application of this connection is the case of the order parameter. For this case, as we also show in Appendix A, equation (4.18) reduces to

$$\lim_{n \rightarrow 0} \frac{\delta}{\delta U_i} ndN\Phi_n(\mu^2, \{U\}) \Big|_{U=0} = \lim_{n \rightarrow 0} \langle Q_i \rangle_{n+1}^P = \left[\frac{1}{N} \sum_{i=1}^N \int_0^1 ds \langle \exp(\mathbf{i}\mathbf{k}^0 \cdot \mathbf{c}_i(s)) \rangle_X \langle \exp(\mathbf{i}\mathbf{k}^1 \cdot \mathbf{c}_i(s)) \rangle_X \cdots \langle \exp(\mathbf{i}\mathbf{k}^g \cdot \mathbf{c}_i(s)) \rangle_X \right], \quad (4.19)$$

where $\hat{l} = \{\mathbf{k}^0, \mathbf{k}^1, \dots, \mathbf{k}^g, \mathbf{0}, \dots, \mathbf{0}\}$, and $\{\mathbf{k}^0, \mathbf{k}^1, \dots, \mathbf{k}^g\}$ are kept fixed as the limit $n \rightarrow 0$ is taken [51]. Similar replica-limit expressions for the disorder average of functions of the quantity (3.1) can also be obtained.

5. Field-theoretic representation

The purpose of the present section is two-fold. First, in sections 5.1 and 5.2 we transform our representation of the physical problem from one expressed in terms of the semi-microscopic replicated macromolecular coordinates to one expressed in terms of generalized monomer densities. These densities are closely related to the order parameter that, as we have seen, diagnoses the various physical states of the system. Then, in sections 5.3 and 5.4, we obtain a field-theoretic representation by applying a sequence of Hubbard–Stratonovich decoupling transformations [8, 9] to the replica-Helmholtz free energy of equation (5.5). This type of decoupling strategy was first used in the context of crosslinked macromolecular systems by Ball and Edwards [6, 7]; see also [52].

The motivation for making these transformations is that they will provide us with a suitable starting point for developing a mean-field description of the transition to and properties of the amorphous solid state. Furthermore, they provide a starting point for the analysis of fluctuations and for the investigation of the elastic properties of the amorphous solid state (see [47]).

5.1. Fourier representation of interactions

At this stage it is useful to introduce the following Fourier representations of the Dirac δ -functions:

$$\delta^{(d)}(\mathbf{c}) = \frac{1}{V} \sum_{\mathbf{p}} \exp(i\mathbf{p} \cdot \mathbf{c}), \quad (5.1 a)$$

$$\delta^{(nd+d)}(\hat{c}) \equiv \prod_{\alpha=0}^n \delta^{(d)}(\mathbf{c}^\alpha) = \frac{1}{V^{n+1}} \sum_{\mathbf{p}^0, \dots, \mathbf{p}^n} \exp\left(i \sum_{\alpha=0}^n \mathbf{p}^\alpha \cdot \mathbf{c}^\alpha\right) \equiv \frac{1}{V^{n+1}} \sum_{\hat{p}} \exp(i\hat{p} \cdot \hat{c}). \quad (5.1 b)$$

Here bold-face wave vectors (such as \mathbf{p}^α) are d -component vectors having components taking on the usual values associated with periodic boundary conditions, i.e. all positive and negative integral multiples of $2\pi/V^{1/d}$ (because $V^{1/d}$ is the length of each side of the d -dimensional cubic container of volume V) [26].

We now introduce a particularly convenient decomposition of the terms in a summation over a replicated wave vector \hat{p} , such as that appearing in equation (5.1 b). Consider a generic replicated vector $\hat{p} \equiv \{\mathbf{p}^0, \mathbf{p}^1, \dots, \mathbf{p}^n\}$. Of the $n+1$ component d -vectors, establish the number h that are non-zero d -vectors. Then we say that the replicated vector \hat{p} resides in the h -replica sector. For example, if $\hat{p} = \{\mathbf{0}, \mathbf{0}, \mathbf{q}^2, \mathbf{0}, \mathbf{q}^4, \mathbf{0}, \mathbf{0}, \dots, \mathbf{0}\}$ with \mathbf{q}^2 and \mathbf{q}^4 both non-zero d -vectors then $h = 2$, and we say that \hat{p} resides in the 2-replica sector. The decomposition that we are introducing amounts to separating from the summation over \hat{p} the term in the 0-replica sector (i.e. the term corresponding to $\hat{p} = \hat{0} \equiv \{\mathbf{0}, \mathbf{0}, \dots, \mathbf{0}\}$), and also separating the terms in the 1-replica sector (i.e. terms corresponding to those values of \hat{p} in which exactly one d -vector is non-zero). Thus we shall decompose summations over \hat{p} into contributions from (i) the 0-replica sector, (ii) the 1-replica sector, and (iii) the remainder, which we refer to as the higher-replica sector, and which contains the h -replica sectors for $2 \leq h \leq n+1$. Schematically, the decomposition can be expressed in the following way:

$$\sum_{\hat{p}} \mathcal{Q}_{\hat{p}} \equiv \mathcal{Q}_{\hat{0}} + \sum_{\alpha=0}^n \sum'_{\mathbf{k}} \mathcal{Q}_{\mathbf{k}}^\alpha + \overline{\sum}_{\hat{k}} \mathcal{Q}_{\hat{k}}. \quad (5.2)$$

Here \sum' denotes a summation over all values of the d -vector \mathbf{k} except that the $\mathbf{k} = \mathbf{0}$ term is omitted (i.e. it comprises terms in the 1-replica sector), $\mathcal{Q}_{\mathbf{k}}^\alpha$ denotes the value of $\mathcal{Q}_{\hat{k}}$ when \hat{k} is in the 1-replica sector (i.e. the α th d -vector entry in \hat{k} is non-zero, all other entries being zero), and $\overline{\sum}_{\hat{k}}$ denotes a summation over replicated vectors \hat{k} residing in the higher replica sector. It will turn out to be useful for us to consider V to be large but (at least initially) finite, in which case it is straightforward to implement the replica-sector decomposition, equation (5.2).

With a view to subsequent decoupling transformations, it is useful to use the Fourier representations of the Dirac δ -functions and the replica-sector decomposition in order to re-express the Dirac δ -function interactions, i.e. the non-Wiener measure terms that couple the replicated degrees of freedom. Thus, we see that the interaction terms in equation (4.1) can be written as

$$\sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \sum_{\alpha=0}^n \delta^{(d)}(\mathbf{c}_i^\alpha(s) - \mathbf{c}_{i'}^\alpha(s'))$$

$$= \frac{N^2}{V} \sum_{\alpha=0}^n \sum_{\mathbf{k}} \left| \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp(i\mathbf{k} \cdot \mathbf{c}_i^\alpha(s)) \right|^2 \quad (5.3 a)$$

$$= \frac{N^2}{V} (n+1) + \frac{N^2}{V} \sum_{\alpha=0}^n \sum'_{\mathbf{k}} \left| \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp(i\mathbf{k} \cdot \mathbf{c}_i^\alpha(s)) \right|^2 \quad (5.3 b)$$

$$= \frac{N^2}{V} (n+1) + \frac{2N^2}{V} \sum_{\alpha=0}^n \sum'_{\mathbf{k}} \dagger \left| \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp(i\mathbf{k} \cdot \mathbf{c}_i^\alpha(s)) \right|^2 \quad (5.3 c)$$

$$= \frac{N^2}{V} (n+1) + \frac{2N^2}{V} \sum_{\alpha=0}^n \sum'_{\mathbf{k}} \dagger |Q_{\mathbf{k}}^\alpha|^2, \quad (5.3 d)$$

$$\sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \prod_{\alpha=0}^n \delta^{(d)}(\mathbf{c}_i^\alpha(s) - \mathbf{c}_{i'}^\alpha(s'))$$

$$= \frac{N^2}{V^{n+1}} \sum_{\hat{\mathbf{k}}} \left| \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp(i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}_i(s)) \right|^2 \quad (5.3 e)$$

$$= \frac{N^2}{V^{n+1}} + \frac{N^2}{V^{n+1}} \sum_{\alpha=0}^n \sum'_{\mathbf{k}} \left| \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp(i\mathbf{k} \cdot \mathbf{c}_i^\alpha(s)) \right|^2$$

$$+ \frac{N^2}{V^{n+1}} \sum_{\hat{\mathbf{k}}} \left| \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp(i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}_i(s)) \right|^2 \quad (5.3 f)$$

$$= \frac{N^2}{V^{n+1}} + \frac{2N^2}{V^{n+1}} \sum_{\alpha=0}^n \sum'_{\mathbf{k}} \dagger \left| \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp(i\mathbf{k} \cdot \mathbf{c}_i^\alpha(s)) \right|^2$$

$$+ \frac{2N^2}{V^{n+1}} \sum_{\hat{\mathbf{k}}} \dagger \left| \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp(i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}_i(s)) \right|^2 \quad (5.3 g)$$

$$= \frac{N^2}{V^{n+1}} + \frac{2N^2}{V^{n+1}} \sum_{\alpha=0}^n \sum'_{\mathbf{k}} \dagger |Q_{\mathbf{k}}^\alpha|^2 + \frac{2N^2}{V^{n+1}} \sum_{\hat{\mathbf{k}}} \dagger |Q_{\hat{\mathbf{k}}}|^2. \quad (5.3 h)$$

For each of the left hand sides we have performed four steps. In the first step we have used equations (5.1 a) and (5.1 b) to re-express the Dirac δ -functions. In the second step we have performed the replica-sector decomposition, according to equation (5.2). In the third step, we have recognized that the summands in the summations over wave vectors of the second step are even functions of the relevant wave vector. Furthermore, none of the summations includes a zero wave vector. Thus, in each case the summation can be restricted to half of the relevant wave vector space, provided a factor of two is included to compensate. To represent this, we have introduced the notation $\sum_{\mathbf{k}} \dagger$ to denote $\sum'_{\mathbf{k}}$ but with \mathbf{k} restricted to the half space via the additional condition $\mathbf{k} \cdot \mathbf{n} > 0$ for a suitable unit d -vector \mathbf{n} , and $\sum_{\hat{\mathbf{k}}} \dagger$ to denote $\sum'_{\hat{\mathbf{k}}}$ but with $\hat{\mathbf{k}}$ restricted to the half space via the additional condition $\hat{\mathbf{k}} \cdot \hat{\mathbf{n}} > 0$ for a suitable unit $(n+1)d$ -vector $\hat{\mathbf{n}}$. The virtue of this procedure is that in our subsequent development it will enable us to avoid the introduction of kinematically

non-independent fields. In the fourth and final step we have used the definition of $Q_{\hat{k}}$ given in equation (4.4), which in the context of the replica-sector decomposition becomes

$$Q_{\mathbf{k}}^{\alpha} \equiv \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp(i\mathbf{k} \cdot \mathbf{c}_i^{\alpha}(s)), \quad (\text{1-replica sector}), \quad (5.4a)$$

$$Q_{\hat{k}} \equiv \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}_i(s)), \quad (\text{higher-replica sector}). \quad (5.4b)$$

5.2. Applications of the Fourier representation

By applying the results of section 5.1 to equation (4.1) we obtain

$\exp(-ndN\Phi_n(\mu^2, \{U\}))$

$$\mathcal{B}_n \left\langle \exp \left(-\frac{\tilde{\lambda}_n^2 N^2}{V} \sum_{\alpha=0}^n \sum_{\mathbf{k}} \dagger |Q_{\mathbf{k}}^{\alpha}|^2 + \frac{\mu^2 N}{V^n} \sum_{\hat{k}} \dagger |Q_{\hat{k}}|^2 - \sum_{\hat{k}} U_{\hat{k}} Q_{\hat{k}} \right) \right\rangle_{n+1}^W, \quad (5.5)$$

$$= \frac{\left\langle \exp \left(-\frac{\tilde{\lambda}_0^2 N^2}{V} \sum_{\mathbf{k}} \dagger |Q_{\mathbf{k}}^0|^2 \right) \right\rangle_1^W}{\left\langle \exp \left(-\frac{\tilde{\lambda}_0^2 N^2}{V} \sum_{\mathbf{k}} \dagger |Q_{\mathbf{k}}^0|^2 \right) \right\rangle_1^W},$$

where we have introduced the effective excluded-volume parameter

$$\tilde{\lambda}_n^2 \equiv \lambda^2 - \frac{\mu^2 V}{NV^n}, \quad (5.6)$$

i.e. the bare excluded-volume parameter λ^2 renormalized to a smaller value by a correction term proportional to the crosslink density parameter μ^2 . The prefactor \mathcal{B}_n is an unimportant constant, which arises from terms in the 0-replica sector, and is given by

$$\mathcal{B}_n \equiv \exp \left(\frac{\mu^2 N}{2V^n} - \frac{\lambda^2 N^2 n}{2v} \right) / \exp \left(\frac{\mu^2 N}{2} \right). \quad (5.7)$$

We see from equations (5.5) and (5.6) that in the 1-replica sector there is a competition between the excluded-volume interaction λ^2 and the effect of the crosslinking, represented by μ^2 . If $\tilde{\lambda}_n^2$ is positive then configurations having non-zero $Q_{\mathbf{k}}^{\alpha}$ are disfavoured (and therefore MTI is favoured), whilst if $\tilde{\lambda}_n^2$ is negative then configurations having non-zero $Q_{\mathbf{k}}^{\alpha}$ are favoured (and therefore there is a tendency to violate MTI). As we are primarily concerned with investigating the liquid and the amorphous solid states, both of which are MTI, we focus our attention on the regime $\tilde{\lambda}_n^2 > 0$. On the other hand, the (higher-replica sector) component of the term due to crosslinking increases the statistical weight of configurations in which $Q_{\hat{k}} \neq 0$ (for \hat{k} in the higher-replica sector). As we shall see in section 6.2, the coefficient of this term, μ^2 , is the control parameter governing the transition from the liquid state (for small μ^2) to the amorphous solid state (for large μ^2), as characterized by the values of the order parameters shown in the table.

5.3. Hubbard–Stratonovich decoupling scheme: replica-Helmholtz free energy at zero external potential

We now obtain a field-theoretic representation by applying a sequence of Hubbard–Stratonovich decoupling transformations to the replica-Helmholtz free energy, equation (5.5). We focus on the case $U = 0$ in the present subsection, and in

Table. Values of the order parameter in the liquid and amorphous solid states.

Sector	Order parameter	Liquid state ($\mu^2 \leq 1$)	Amorphous solid state ($\mu^2 > 1$)
One-replica	$\langle Q_{\mathbf{k}}^\alpha \rangle_{n+1}^P$	= 0	= 0
Higher-replica	$\langle Q_{\hat{k}} \rangle_{n+1}^P$	= 0	$\neq 0$

the following subsection present results that allow for non-zero U . The motivation for these transformations is that via them all interactions between different macromolecules are eliminated at the expense of introducing a certain additional stochastic field to which the monomers are coupled. This strategy has the following virtues. First, the task of summing over the configurations of the system of N replicated macromolecules is reduced to the task of summing over the configurations of a *single* replicated macromolecule, albeit one that is coupled to the stochastic field. The monomers that constitute this replicated macromolecule remain coupled to each other via the Wiener measure, equation (2.2), and by the stochastic field to which they are coupled. To the extent that this summation can be performed, equation (5.12 a) gives the replica-Helmholtz free energy in terms of functional integrals over the stochastic fields. Second, the stochastic field itself has a natural physical interpretation: as we shall see explicitly in section 5.4 it is related in a direct manner to the order parameter.

The appropriate Hubbard–Stratonovich decoupling transformations are predicted on the multiple use of the following pair of integrals:

$$\exp(-a|w|^2) = (a/\pi) \int d(\text{Re } z) d(\text{Im } z) \exp(-a|z|^2) \exp(2ia \text{Re } zw^*), \quad (5.8 a)$$

$$\exp(+a|w|^2) = (a/\pi) \int d(\text{Re } z) d(\text{Im } z) \exp(-a|z|^2) \exp(2a \text{Re } zw^*). \quad (5.8 b)$$

Here w is an arbitrary complex number, a is a real and positive (but otherwise arbitrary) number, and the integrals are taken over the entire complex z plane. We transform each exponential term inside an expectation value in equation (5.5) (with $U = 0$) by using these integrals, those having the coefficient $\tilde{\lambda}_n^2$ or $\tilde{\lambda}_0^2$ with equation (5.8 a) and those having the coefficient μ^2 with equation (5.8 b).

We define the measures \mathcal{D}_n^\dagger , \mathcal{D}^\dagger and \mathcal{D}_0^\dagger via

$$\mathcal{D}_n^\dagger \Omega \equiv \prod_{\alpha=0}^n \prod_{\mathbf{k}} \int \frac{\tilde{\lambda}_n^2 N^2}{\pi V} d(\text{Re } \Omega_{\mathbf{k}}^\alpha) d(\text{Im } \Omega_{\mathbf{k}}^\alpha), \quad (5.9 a)$$

$$\mathcal{D}^\dagger \Omega \equiv \prod_{\hat{k}} \int \frac{\mu^2 N}{\pi V^n} d(\text{Re } \Omega_{\hat{k}}) d(\text{Im } \Omega_{\hat{k}}), \quad (5.9 b)$$

$$\mathcal{D}_0^\dagger \omega \equiv \prod_{\mathbf{k}} \int \frac{\tilde{\lambda}_0^2 N^2}{\pi V} d(\text{Re } \omega_{\mathbf{k}}) d(\text{Im } \omega_{\mathbf{k}}), \quad (5.9 c)$$

where $\prod_{\mathbf{k}}^\dagger$ denotes the product over all d -vectors \mathbf{k} in the half-space given by the condition $\mathbf{k} \cdot \mathbf{n} > 0$ for a suitable unit d -vector \mathbf{n} , and $\prod_{\hat{k}}^\dagger$ denotes the product over all $(n + 1)d$ -vectors \hat{k} in the half-space given by the condition $\hat{k} \cdot \hat{n} > 0$ for a suitable unit $(n + 1)d$ -vector \hat{n} . These definitions have convenient normalization properties [53]:

$$\int \mathcal{D}_n^\dagger \Omega \exp \left(-\tilde{\lambda}_n^2 N^2 V^{-1} \sum_{\alpha=0}^n \sum_{\mathbf{k}}^\dagger |\Omega_{\mathbf{k}}^\alpha|^2 \right) = 1, \quad (5.10 a)$$

$$\int \bar{\mathcal{D}}^\dagger \Omega \exp \left(-\mu^2 N V^{-n} \sum_{\hat{k}}^\dagger |\Omega_{\hat{k}}|^2 \right) = 1, \quad (5.10 b)$$

$$\int \mathcal{D}_0^\dagger \omega \exp \left(-\tilde{\lambda}_0^2 N^2 V^{-1} \sum_{\mathbf{k}}^\dagger |\omega_{\mathbf{k}}|^2 \right) = 1. \quad (5.10 c)$$

By using this sequence of Hubbard–Stratonovich transformations, equation (5.5) becomes

$$\exp(-ndN\Phi_n(\mu^2, \{0\})) =$$

$$\begin{aligned} & \mathcal{B}_n \int \mathcal{D}_n^\dagger \Omega \exp \left(-\tilde{\lambda}_n^2 N^2 V^{-1} \sum_{\alpha=0}^n \sum_{\mathbf{k}}^\dagger |\Omega_{\mathbf{k}}^\alpha|^2 \right) \int \bar{\mathcal{D}}^\dagger \Omega \exp \left(-\mu^2 N V^{-n} \sum_{\hat{k}}^\dagger |\Omega_{\hat{k}}|^2 \right) \\ & \times \left\langle \exp \left(2i\tilde{\lambda}_n^2 N^2 V^{-1} \sum_{\alpha=0}^n \sum_{\mathbf{k}}^\dagger \text{Re} \Omega_{\mathbf{k}}^{\alpha*} Q_{\mathbf{k}}^\alpha + 2\mu^2 N V^{-n} \sum_{\hat{k}}^\dagger \text{Re} \Omega_{\hat{k}}^* Q_{\hat{k}} \right) \right\rangle_{n+1}^W \\ & \frac{\int \mathcal{D}_0^\dagger \omega \exp \left(-\tilde{\lambda}_0^2 N^2 V^{-1} \sum_{\mathbf{k}}^\dagger |\omega_{\mathbf{k}}|^2 \right) \left\langle \exp \left(2i\tilde{\lambda}_0^2 N^2 V^{-1} \sum_{\mathbf{k}}^\dagger \text{Re} \omega_{\mathbf{k}}^* Q_{\mathbf{k}}^0 \right) \right\rangle_1^W}{\int \mathcal{D}_0^\dagger \omega \exp \left(-\tilde{\lambda}_0^2 N^2 V^{-1} \sum_{\mathbf{k}}^\dagger |\omega_{\mathbf{k}}|^2 \right)}. \end{aligned} \quad (5.11)$$

By examining the expectation values $\langle \dots \rangle_{n+1}^W$ and $\langle \dots \rangle_1^W$ in equation (5.11) we see that indeed the sequence of Hubbard–Stratonovich transformations has led to the decoupling of the N (replicated) macromolecules from each other. Moreover, as these expectation values are products of identical factors, one for each replicated macromolecule, we may replace them by the N th power of an expectation value involving a single replicated macromolecule. Thus, we see that equation (5.5) is given by the quotient of partition functions of stochastic fields,

$$\exp(-ndN\Phi_n(\mu^2, \{0\})) = \mathcal{B}_n \frac{\int \mathcal{D}_n^\dagger \Omega \int \bar{\mathcal{D}}^\dagger \Omega \exp(-ndN\mathcal{F}_n(\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\}))}{\int \mathcal{D}_0^\dagger \omega \exp(-ndN\mathcal{F}^{\text{den}}(\{\omega_{\mathbf{k}}\}))}, \quad (5.12 a)$$

governed by the effective Hamiltonians $\mathcal{F}_n(\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\})$ and $\mathcal{F}^{\text{den}}(\{\omega_{\mathbf{k}}\})$, where

$$\begin{aligned} nd\mathcal{F}_n(\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\}) & \equiv \tilde{\lambda}_n^2 N V^{-1} \sum_{\alpha=0}^n \sum_{\mathbf{k}}^\dagger |\Omega_{\mathbf{k}}^\alpha|^2 + \mu^2 V^{-n} \sum_{\hat{k}}^\dagger |\Omega_{\hat{k}}|^2 \\ & - \ln \left\langle \exp \left\{ 2i\tilde{\lambda}_n^2 N V^{-1} \sum_{\alpha=0}^n \sum_{\mathbf{k}}^\dagger \text{Re} \Omega_{\mathbf{k}}^{\alpha*} \int_0^1 ds \exp(i\mathbf{k} \cdot \mathbf{c}^\alpha(s)) \right\} \right. \\ & \left. \times \exp \left\{ 2\mu^2 V^{-n} \sum_{\hat{k}}^\dagger \text{Re} \Omega_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \right\rangle_{n+1}^W, \end{aligned} \quad (5.12 b)$$

$$\begin{aligned}
 nd\mathcal{F}^{\text{den}}(\{\omega_{\mathbf{k}}\}) & \\
 \equiv \bar{\lambda}_0^2 NV^{-1} \sum_{\mathbf{k}}^\dagger |\omega_{\mathbf{k}}|^2 - \ln \left\langle \exp \left\{ 2i\bar{\lambda}_0^2 NV^{-1} \sum_{\mathbf{k}}^\dagger \text{Re } \omega_{\mathbf{k}}^* \int_0^1 ds \exp(i\mathbf{k} \cdot \mathbf{c}(s)) \right\} \right\rangle_1^W. & \quad (5.12c)
 \end{aligned}$$

We can compute $\mathcal{F}_n(\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\})$ and $\mathcal{F}^{\text{den}}(\{\omega_{\mathbf{k}}\})$ perturbatively [54], order by order, in powers of $\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\}$ and $\{\omega_{\mathbf{k}}\}$. This perturbative construction of the Landau–Ginzburg–Wilson effective Hamiltonian is equivalent to that arising in many other contexts in statistical physics.

5.4. Hubbard–Stratonovich decoupling scheme: replica-Helmholtz free energy at non-zero external potential

We now turn to the general case of the replica-Helmholtz free energy, in which U need not vanish. As with the $U = 0$ case, it will be convenient to perform a Hubbard–Stratonovich decoupling transformation on $\Phi_n(\mu^2, \{U\})$. This transformation is predicated on the multiple use of the following pair of integrals, which are generalizations of those given in equations (5.8 a) and (5.8 b):

$$\begin{aligned}
 \exp(-a(|w|^2 - jw - \bar{j}w^*)) & \\
 = (a/\pi) \exp(aj\bar{j}) \int d(\text{Re } z) d(\text{Im } z) \exp(-a|z|^2 + 2ia \text{Re } zw^* - ia(zj + z^*\bar{j})), & \quad (5.13a)
 \end{aligned}$$

$$\begin{aligned}
 \exp(a|w|^2 - jw - \bar{j}w^*) & \\
 = (a/\pi) \exp(-aj\bar{j}) \int d(\text{Re } z) d(\text{Im } z) \exp(-a|z|^2 + 2a \text{Re } zw^* - a(zj + z^*\bar{j})). & \quad (5.13b)
 \end{aligned}$$

Here w, j and \bar{j} are arbitrary complex numbers, a is a real and positive (but otherwise arbitrary) number, and the integrals are taken over the entire complex z plane. Following a strategy analogous to that used for the $U = 0$ case, we find

$$\begin{aligned}
 ndN\Phi_n(\mu^2, \{U\}) & = -\ln \mathcal{Z}_n + \ln \int \mathcal{D}_0^\dagger \omega \exp(-ndN\mathcal{F}^{\text{den}}(\{\omega_{\mathbf{k}}\})) \\
 & - \frac{V}{N^2 \bar{\lambda}_n^2} \sum_{\alpha=0}^n \sum_{\mathbf{k}}^\dagger U_{\mathbf{k}}^\alpha U_{-\mathbf{k}}^\alpha + \frac{V^n}{N\mu^2} \sum_{\hat{k}}^\dagger U_{\hat{k}} U_{-\hat{k}} \\
 & - \ln \int \mathcal{D}_n^\dagger \Omega \bar{\mathcal{D}}^\dagger \Omega \exp\left(-ndN\mathcal{F}_n(\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\})\right) \\
 & + i \sum_{\alpha=0}^n \sum_{\mathbf{k}}' U_{\mathbf{k}}^\alpha \Omega_{\mathbf{k}}^\alpha - \sum_{\hat{k}} U_{\hat{k}} \Omega_{\hat{k}}, \quad (5.14)
 \end{aligned}$$

where the effective Hamiltonian \mathcal{F}_n is given in equation (5.12 b). Thus we have transformed our description into an effective one for the fields $\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\}$. It should be noted that the coefficients of the powers of $\{U_{\mathbf{k}}^\alpha, U_{\hat{k}}\}$ in the functional Taylor series for $\Phi_n(\mu^2, \{U\})$ are simply related to the connected correlators of $\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\}$ via

$$\begin{aligned}
ndN\Phi_n(\mu^2, \{U\}) &= ndN\Phi_n(\mu^2, \{0\}) - \frac{V}{2N^2\tilde{\chi}_n^2} \sum_{\alpha=0}^n \sum_{\mathbf{k}}' U_{\mathbf{k}}^\alpha U_{-\mathbf{k}}^\alpha + \frac{V^n}{2N\mu^2} \sum_{\hat{k}} U_{\hat{k}} U_{-\hat{k}} \\
&+ \sum_{r,s=0; (r,s) \neq (0,0)}^{\infty} \frac{i^r (-1)^{s+1}}{r! s!} \sum_{\alpha_1=0}^n \sum_{\mathbf{k}_1}' \dots \sum_{\alpha_r=0}^n \sum_{\mathbf{k}_r}' \sum_{\hat{k}_1}' \dots \\
&\times \sum_{\hat{k}_s} U_{\mathbf{k}_1}^{\alpha_1} \dots U_{\mathbf{k}_r}^{\alpha_r} U_{\hat{k}_1} \dots U_{\hat{k}_s} \langle \Omega_{\mathbf{k}_1}^{\alpha_1} \dots \Omega_{\mathbf{k}_r}^{\alpha_r} \Omega_{\hat{k}_1} \dots \Omega_{\hat{k}_s} \rangle_{n+1, \mathcal{C}}, \quad (5.15 a)
\end{aligned}$$

where the expectation value $\langle \dots \rangle_{n+1}^{\mathcal{C}}$ is defined via

$$\langle \dots \rangle_{n+1}^{\mathcal{C}} \equiv \frac{\int \mathcal{D}_n^\dagger \Omega \mathcal{D}_n^\dagger \Omega \dots \exp(-ndN\mathcal{F}_n(\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\}))}{\int \mathcal{D}_n^\dagger \Omega \mathcal{D}_n^\dagger \Omega \exp(-ndN\mathcal{F}_n(\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\}))}. \quad (5.15 b)$$

The virtue of the present development is that it allows us to construct quantities of physical interest, which typically involve the densities $\{Q_{\mathbf{k}}^\alpha, Q_{\hat{k}}\}$ in terms of more readily computable quantities, which involve the stochastic fields $\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\}$. Indeed, by using equations (4.17) and (5.15 a) we see that

$$\langle Q_{\mathbf{k}}^\alpha \rangle_{n+1}^{\mathcal{P}} = -i \langle \Omega_{\mathbf{k}}^\alpha \rangle_{n+1}^{\mathcal{C}}, \quad (5.16 a)$$

$$\langle Q_{\hat{k}} \rangle_{n+1}^{\mathcal{P}} = \langle \Omega_{\hat{k}} \rangle_{n+1}^{\mathcal{C}}. \quad (5.16 b)$$

Thus, by using equation (4.19) we see that we can relate the order parameter to the expectation value of the stochastic field $\Omega_{\hat{k}}$ as

$$\left[\frac{1}{N} \sum_{i=1}^N \int_0^1 ds \langle \exp(i\mathbf{k}^0 \cdot \mathbf{c}_i(s)) \rangle_\chi \langle \exp(i\mathbf{k}^1 \cdot \mathbf{c}_i(s)) \rangle_\chi \dots \langle \exp(i\mathbf{k}^g \cdot \mathbf{c}_i(s)) \rangle_\chi \right] = \lim_{n \rightarrow 0} \langle \Omega_{\hat{l}} \rangle_{n+1}^{\mathcal{C}}, \quad (5.17)$$

where $\hat{l} = \{\mathbf{k}^0, \mathbf{k}^1, \dots, \mathbf{k}^g, \mathbf{0}, \dots, \mathbf{0}\}$. In the following section we make explicit use of this development in order to compute the order parameter.

6. Saddle-point approximation in the critical regime

In the preceding sections we have developed an exact, formal, field-theoretic representation of the statistical mechanics of randomly crosslinked macromolecular networks. In the present section we shall explore the properties of such systems, focusing our attention on the regime of crosslink densities near to the equilibrium phase transition from the liquid state to the amorphous solid state that sufficient crosslinking causes. We shall do this by analysing the field-theoretic representation at the level of mean-field theory, considering in detail expressions for the free energy and the order parameter. Following this, in section 7, we shall consider the implications of a certain, physically important class of fluctuations. In order to streamline the presentation, a considerable amount of technical detail has been

relegated to the Appendices. The main results of this section have been briefly reported in [13].

6.1. Approximation strategy

The mean-field level of approximation follows from computing the functional integral in the numerator of equation (5.12 a) by using the saddle-point method. This amounts to replacing the functional integral by the value of its integrand that is stationary with respect to variations of $\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\}$, so that, omitting unimportant constants, we obtain the following approximations for $\Phi_n(\mu^2, \{0\})$, $\langle \Omega_{\mathbf{k}}^\alpha \rangle_{n+1}^{\mathcal{F}}$, $\langle \Omega_{\hat{k}} \rangle_{n+1}^{\mathcal{F}}$ and $\langle q \rangle_{n+1}^{\mathcal{P}}$:

$$\Phi_n(\mu^2, \{0\}) = \mathcal{F}_n(\{\bar{\Omega}_{\mathbf{k}}^\alpha, \bar{\Omega}_{\hat{k}}\}), \quad (6.1 a)$$

$$i\langle Q_{\mathbf{k}}^\alpha \rangle_{n+1}^{\mathcal{P}} = \langle \Omega_{\mathbf{k}}^\alpha \rangle_{n+1}^{\mathcal{F}} = \bar{\Omega}_{\mathbf{k}}^\alpha, \quad (6.1 b)$$

$$\langle Q_{\hat{k}} \rangle_{n+1}^{\mathcal{P}} = \langle \Omega_{\hat{k}} \rangle_{n+1}^{\mathcal{F}} = \bar{\Omega}_{\hat{k}}. \quad (6.1 c)$$

Here $\bar{\Omega}_{\mathbf{k}}^\alpha$ and $\bar{\Omega}_{\hat{k}}$ make $\mathcal{F}_n(\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\})$ stationary, i.e. satisfy the stationarity conditions

$$\left. \frac{\delta \mathcal{F}_n}{\delta \Omega_{\mathbf{q}}^{\alpha*}} \right|_{\{\bar{\Omega}_{\mathbf{k}}^\alpha, \bar{\Omega}_{\hat{k}}\}} = 0, \quad (6.2 a)$$

$$\left. \frac{\delta \mathcal{F}_n}{\delta \Omega_{\hat{q}}} \right|_{\{\bar{\Omega}_{\mathbf{k}}^\alpha, \bar{\Omega}_{\hat{k}}\}} = 0. \quad (6.2 b)$$

By using equation (5.12 b) the stationarity conditions become

$$\begin{aligned} \bar{\Omega}_{\mathbf{q}}^\alpha = & \frac{i \left\langle \int_0^1 dt \exp(i\mathbf{q} \cdot \mathbf{c}^\alpha(t)) \exp \left\{ 2i\bar{\lambda}_n^2 NV^{-1} \sum_{\alpha=0}^n \sum_{\mathbf{k}} \dagger \operatorname{Re} \bar{\Omega}_{\mathbf{k}}^{\alpha*} \int_0^1 ds \exp(i\mathbf{k} \cdot \mathbf{c}^\alpha(s)) \right\} \right. \\ & \times \exp \left\{ 2\mu^2 V^{-n} \sum_{\hat{k}} \dagger \operatorname{Re} \bar{\Omega}_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \left. \right\rangle_{n+1}^{\mathcal{W}}}{\left\langle \exp \left\{ 2i\bar{\lambda}_n^2 NV^{-1} \sum_{\alpha=0}^n \sum_{\mathbf{k}} \dagger \operatorname{Re} \bar{\Omega}_{\mathbf{k}}^{\alpha*} \int_0^1 ds \exp(i\mathbf{k} \cdot \mathbf{c}^\alpha(s)) \right\} \right. \\ & \times \exp \left\{ 2\mu^2 V^{-n} \sum_{\hat{k}} \dagger \operatorname{Re} \bar{\Omega}_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \left. \right\rangle_{n+1}^{\mathcal{W}}}, \end{aligned} \quad (6.3 a)$$

$$\bar{\Omega}_{\hat{q}} = \frac{\left\langle \int_0^1 dt \exp(i\hat{q} \cdot \hat{c}(t)) \exp \left\{ 2i\bar{\lambda}_n^2 NV^{-1} \sum_{\alpha=0}^n \sum_{\mathbf{k}} \dagger \operatorname{Re} \bar{\Omega}_{\mathbf{k}}^{\alpha*} \int_0^1 ds \exp(i\mathbf{k} \cdot \mathbf{c}^\alpha(s)) \right\} \right.}{\left\langle \exp \left\{ 2i\bar{\lambda}_n^2 NV^{-1} \sum_{\alpha=0}^n \sum_{\mathbf{k}} \dagger \operatorname{Re} \bar{\Omega}_{\mathbf{k}}^{\alpha*} \int_0^1 ds \exp(i\mathbf{k} \cdot \mathbf{c}^\alpha(s)) \right\} \right.} \times \exp \left\{ 2\mu^2 V^{-n} \sum_{\hat{k}} \dagger \operatorname{Re} \bar{\Omega}_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \Bigg\rangle_{n+1}^W$$

$$\times \exp \left\{ 2\mu^2 V^{-n} \sum_{\hat{k}} \dagger \operatorname{Re} \bar{\Omega}_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \Bigg\rangle_{n+1}^W \quad (6.3 b)$$

6.2. Instability of the liquid state

In the context of the mean-field approximation, the liquid state corresponds to $\bar{\Omega}_{\mathbf{k}}^\alpha = \bar{\Omega}_{\hat{k}} = 0$, which can readily be checked to solve equations (6.3 a) and (6.3 b). To address the stability of this state we examine $\mathcal{F}_n(\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\})$, equation (5.12 b), and expand perturbatively about $\Omega_{\mathbf{k}}^\alpha = \Omega_{\hat{k}} = 0$ to second order in $\Omega_{\mathbf{k}}^\alpha$ and $\Omega_{\hat{k}}$. This gives

$$nd\mathcal{F}_n(\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\}) = \bar{\lambda}_n^2 NV^{-1} \sum_{\alpha=0}^n \sum_{\mathbf{k}} \dagger (1 + \bar{\lambda}_n^2 NV^{-1} g_0(|\mathbf{k}|^2)) |\Omega_{\mathbf{k}}^\alpha|^2 + \mu^2 V^{-n} \sum_{\hat{k}} \dagger (1 - \mu^2 V^{-n} g_0(|\hat{k}|^2)) |\Omega_{\hat{k}}|^2 + \dots \quad (6.4)$$

The correlators necessary to calculate the terms in this expansion are computed in Appendix B, and the function $g_0(|\mathbf{k}|^2)$ resulting from the subsequent arclength integrations is defined in Appendix C, and has the value

$$g_0(|\mathbf{k}|^2) = \frac{e^{-k^2/2} - (1 - \frac{1}{2}k^2)}{\frac{1}{2}(\frac{1}{2}k^2)^2} \sim \begin{cases} 1 - k^2/6, & \text{if } k^2 \ll 1; \\ 4/k^2, & \text{if } k^2 \gg 1. \end{cases}$$

As we anticipated at the end of section 5.2, the stability of the 1-replica sector is controlled by the coefficient of the $|\Omega_{\mathbf{k}}^\alpha|^2$ term in this expansion. This coefficient, together with the positive definiteness of $g_0(|\mathbf{k}|^2)$, show that provided the crosslink-renormalized excluded-volume parameter $\bar{\lambda}_n^2$, given in equation (5.6), is positive, the 1-replica sector is locally stable. Thus, the saddle-point value $\bar{\Omega}_{\mathbf{k}}^\alpha$ is zero. The positive definiteness of $\bar{\lambda}_n^2$ requires that

$$\lambda^2 > \frac{\mu^2 V}{NV^n}, \quad (6.5)$$

i.e. that the repulsive character of the physical excluded-volume parameter λ^2 is sufficiently strong to enable the system to withstand the effective tendency towards collapse afforded by the crosslinking. Thus, we see that even at the level of mean-field theory it is only as a consequence of the presence of the excluded-volume interaction that the system can, at the same time, be stable with respect to collapse to the (inhomogeneous) globular state and yet unstable with respect to the formation of the (macroscopically homogeneous) amorphous solid state.

The stability of the higher-replica sector is controlled by the coefficient of the $|\Omega_{\hat{k}}|^2$ term in the expansion, equation (6.4), i.e. by

$$1 - \mu^2 V^{-n} g_0(|\hat{k}|^2), \quad (6.6)$$

(considering, as we do, $\mu^2 \geq 0$). The two contributions to this coefficient enter with competing signs, owing to the attractive nature of the effective term arising from crosslinking, and thus provide the opportunity for the loss of positivity of this coefficient. Indeed, the coefficient indicates that the liquid state will be stable for $\mu^2 < 1$ and unstable for $\mu^2 > 1$, i.e. stable only for sufficiently small crosslink density, the factor of V^{-n} in equation (6.6) being eliminated by first taking the limit $n \rightarrow 0$, and subsequently taking the thermodynamic limit ($V \rightarrow \infty$, $N \rightarrow \infty$, N/V fixed, μ^2 fixed) [55]. The least stable modes correspond to long wavelengths, $\hat{k}^2 \rightarrow 0$, for which $g_0(|\hat{k}|^2) \rightarrow 1$ from below [56].

The linear stability analysis of the present subsection indicates that the liquid state, as characterized by the order parameter discussed in section 3, is stable when the mean number of crosslinks per macromolecule $[M]/N$ is smaller than a certain critical value M_c/N , i.e. those mean crosslink densities corresponding to $\mu^2 < 1$. However, for larger crosslink densities, $([M]/N) > (M_c/N)$, i.e. $\mu^2 > 1$, the liquid state is unstable [57], being replaced by an alternative state which, as we shall see in the following two subsections, is an amorphous solid state, characterized by $\Omega_{\hat{k}} \neq 0$ but $\Omega_{\mathbf{k}}^\alpha = 0$. In fact, the state that replaces the liquid state will turn out to have the property of macroscopic translational invariance (see section 3.1), so that even though it has $\Omega_{\hat{k}} \neq 0$, this is compatible with and does not disturb the fact that the 1-replica sector remains stable and that $\Omega_{\mathbf{k}}^\alpha$ remains zero.

6.3. Free energy

We now set about exploring the nature of the amorphous solid state with respect to which the liquid state is unstable for $\mu^2 > 1$. Initially, we do this by following the strategy outlined in section 6.1 of making \mathcal{F}_n stationary with respect to the fields $\Omega_{\mathbf{k}}^\alpha$ and $\Omega_{\hat{k}}$. However, we are unable to parametrize the entire space of possible fields. Instead, we consider the class of fields for which physical motivation was presented in section 3.2 (see equation (3.14)),

$$\Omega_{\mathbf{k}}^\alpha = 0, \quad (1\text{-replica sector}), \quad (6.7a)$$

$$\Omega_{\hat{k}} = q \delta_{\hat{k},0}^{(d)} \int_0^\infty d\tau p(\tau) \exp(-\hat{k}^2/2\tau), \quad (\text{higher-replica sector}), \quad (6.7b)$$

evaluate \mathcal{F}_n for such fields, and make the resulting quantity stationary with respect to the variational quantities, the gel fraction q (a number) and the distribution of (inverse square) localization lengths $p(\tau)$ (a normalized function). This amounts to making a variational mean-field approximation. However, as we shall see in the following subsection, the hypothesis we make for the saddle point will actually turn out to contain an exact saddle point of \mathcal{F}_n .

By inspecting equation (5.12b) and employing equation (6.7a) we see that there are two contributions to the free energy: a term quadratic in $\Omega_{\hat{k}}$, and a term that can be identified as the logarithm of the partition function of a single replicated macromolecule coupled to $\Omega_{\hat{k}}$. The explicit details of the evaluation of these terms when $\Omega_{\hat{k}}$ is given by equation (6.7b) is presented in Appendix D. Then the variational mean-field approximation to the free energy is given by

$$\tilde{f} = \lim_{n \rightarrow 0} \Phi_n(\mu^2, \{0\}) \approx \lim_{n \rightarrow 0} \min_{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}} \mathcal{F}_n(\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}\}) \approx \min_{q, p(\tau)} \tilde{f}^{\text{var}}\{q, p\}, \quad (6.8)$$

where we have omitted constants independent of the variational parameters q and

$p(\tau)$, and the variational free energy $\tilde{f}^{\text{var}}\{q, p\}$ is given by

$$\begin{aligned} \tilde{f}^{\text{var}}\{q, p\} = & -\frac{1}{2}(\exp(-\mu^2 q) - (1 - \mu^2 q) - \frac{1}{2}\mu^2 q^2) \ln(V^{2/d}/2\pi e) \\ & + \frac{1}{4}\mu^2 q^2 \int_0^\infty d\tau_1 p(\tau_1) \int_0^\infty d\tau_2 p(\tau_2) \ln((\tau_1^{-1} + \tau_2^{-2})^{-1}) \\ & + \frac{1}{2} \exp(-\mu^2 q) \sum_{r=1}^\infty \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_r \\ & \times \int_0^\infty d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \ln(\mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}_{\rho\rho'}^{(r)}). \end{aligned} \quad (6.9)$$

Here $\text{Det}^{(r)}$ denotes the determinant of an $r \times r$ matrix, $\mathcal{R}_{\rho\rho'}^{(r)}$ is an $(r \times r)$ -matrix-valued function of the r arclength coordinates $\{s_\nu\}_{\nu=1}^r$ and the r inverse square localization lengths $\{\tau_\nu\}_{\nu=1}^r$, and $\mathcal{W}^{(r)}$ is a single such function, $\mathcal{R}_{\rho\rho'}^{(r)}$ and $\mathcal{W}^{(r)}$ being respectively defined in equations (F1) and (F2 b) of Appendix F.

As anticipated in section 2.6, in addition to intensive terms we find a non-intensive term, proportional to $\ln V$, owing to the omission of the disorder average of the Gibbs symmetry factor. The presence of the $\ln V$ factor signals the fact that the configuration integral produces additional powers of V . These powers of V can only be due to degrees of freedom that are allowed to vary over the entire sample, i.e. to the fraction of macromolecules that are delocalized. Thus this term depends on the gel fraction q , but it cannot (and does not) depend on $p(\tau)$, which only describes the localized degrees of freedom. In the following subsection we shall analyse the self-consistency condition for the order parameter directly and, although no quantity proportional to $\ln V$ will appear, we will re-obtain the exact same results as in the present subsection. This approach will be seen to have the additional substantial virtue of demonstrating that the hypothesized form of the order parameter, equation (3.14), used in the present section as a variational hypothesis, in fact provides an *exact saddle point* of the free energy, not merely a variational approximation.

As a first step towards minimizing \tilde{f}^{var} we regard the term proportional to $\ln V$ as dominant, and make it stationary with respect to the gel fraction q . This leads to the condition [58, 34, 13]

$$\exp(-\mu^2 q) = 1 - q. \quad (6.10)$$

For all values of μ^2 this equation has the root $q = 0$, corresponding to the liquid state. However, for $\mu^2 > 1$ an additional root appears, emerging continuously from $q = 0$ at $\mu^2 = 1$, and describing the equilibrium amorphous solid state. In figure 1 we show the dependence of the gel fraction on μ^2 . For $\mu^2 \gg 1$, i.e. the highly crosslinked regime, q approaches unity asymptotically as $q \sim 1 - \exp(-\mu^2)$. In the critical regime, $0 \leq \mu^2 - 1 \ll 1$, it is convenient to exchange μ^2 for the new control parameter ϵ , defined via

$$\mu^2 \equiv 1 + \epsilon/3, \quad (6.11)$$

with $0 \leq \epsilon \ll 1$. We may then solve perturbatively for q , obtaining

$$q = 2\epsilon/3 + \mathcal{O}(\epsilon^2). \quad (6.12)$$

Having determined the condition satisfied by q we now turn our attention to the dependence of \tilde{f}^{var} on the distribution $p(\tau)$ of inverse square localization lengths. As we are primarily interested in crosslink densities in the vicinity of the vulcanization transition (i.e. $0 \leq \epsilon \ll 1$), we use the result that, to order ϵ , we have $q = 2\epsilon/3$. This

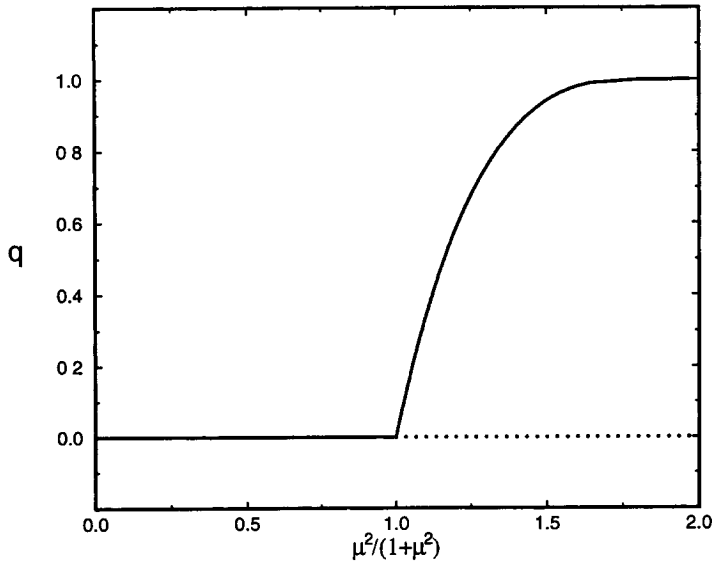


Figure 1. Dependence of the gel fraction q on μ^2 : stable solution (full line); unstable solution (dotted line).

allows us to retain in the summation over r in equation (6.9) only the terms $r = 2, 3$ (the $r = 1$ term vanishing identically by the construction of $\mathcal{W}^{(r)}$). Next, we assume that the inverse square localization lengths having appreciable statistical weight in $p(\tau)$ are also of order ϵ , i.e. small compared to unity, in units such that $(\ell L/d)^{1/2} = 1$, so that localization is on length scales much larger than the size of a free macromolecule. (We shall confirm the consistency of this assumption *a posteriori*.) Thus, we may use the result from Appendix F to expand $\ln(\mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{G}_{\rho\rho'})$ in equation (6.9) for small $\{\tau_\rho\}_{\rho=1}^r$, retaining terms to order τ_ρ . Then we integrate over the arclength variables $\{s_1, \dots, s_r\}$ by using the results of Appendix F. Omitting terms that are independent of $p(\tau)$ we find that, to $\mathcal{O}(\epsilon^3)$,

$$\begin{aligned} \tilde{f}^{\text{var}} = & -\frac{1}{8} \left(\frac{2\epsilon}{3}\right)^3 \left\{ \ln \left(\frac{\tau_1 + \tau_2}{\tau_1 \tau_2} \right) \right\}_\tau + \frac{1}{12} \left(\frac{2\epsilon}{3}\right)^3 \left\{ \ln \left(\frac{\tau_1 + \tau_2 + \tau_3}{\tau_1 \tau_2 \tau_3} \right) \right\}_\tau \\ & + \frac{1}{12} \left(\frac{2\epsilon}{3}\right)^2 \left\{ \frac{\tau_1 \tau_2}{\tau_1 + \tau_2} \right\}_\tau, \end{aligned} \quad (6.13)$$

where the brace carrying the subscript τ indicates averaging over the localization lengths, i.e. $\{\Psi(\tau_1, \tau_2, \dots)\}_\tau \equiv \int_0^\infty d\tau_1 p(\tau_1) d\tau_2 p(\tau_2) \dots \Psi(\tau_1, \tau_2, \dots)$, as many lengths τ_1, τ_2, \dots as feature as arguments of the arbitrary function Ψ .

For future reference we note that if we suppose that the distribution of localization lengths is sharp, i.e. has no fluctuations, so that $\rho(\tau) = \delta(\tau - \xi^{-2})$, where ξ is the sharp value of the localization lengths, then the expression for \tilde{f}^{var} simplifies, becoming

$$\tilde{f}^{\text{var}} = \frac{1}{24} \left(\frac{2\epsilon}{3}\right)^3 \ln(\xi^2) + \frac{1}{24} \left(\frac{2\epsilon}{3}\right)^2 \frac{1}{\xi^2}, \quad (6.14)$$

correct to $\mathcal{O}(\epsilon^3)$. In this case, demanding that \tilde{f}^{var} be stationary with respect to ξ^2 yields, to $\mathcal{O}(\epsilon)$,

$$\frac{1}{\xi^2} = \begin{cases} 0, & \text{if } \mu^2 \leq 1, \\ 2\epsilon/3, & \text{if } \mu^2 \geq 1. \end{cases} \quad (6.15)$$

We now return to the general situation, in which the distribution of localization lengths is not constrained to be sharp. Rather than demand that \tilde{f}^{var} be explicitly stationary with respect to $p(\tau)$ itself, it is convenient to exchange its dependence on $p(\tau)$ for dependence on the Laplace transform $\hat{p}(\hat{\tau})$, given by

$$\hat{p}(\hat{\tau}) \equiv \int_0^\infty d\tau p(\tau) \exp(-\hat{\tau}\tau). \quad (6.16)$$

The details of this exchange are deferred to Appendix H; what results is the following expression for \tilde{f}^{var} , correct to $\mathcal{O}(\epsilon^3)$:

$$\begin{aligned} \tilde{f}^{\text{var}} = & -\frac{1}{8} \left(\frac{2\epsilon}{3}\right)^3 \int_0^\infty \frac{d\hat{\tau}}{\hat{\tau}} [-\hat{p}(\hat{\tau})^2 + 2\hat{p}(\hat{\tau}) - \exp(-\hat{\tau})] \\ & + \frac{1}{12} \left(\frac{2\epsilon}{3}\right)^3 \int_0^\infty \frac{d\hat{\tau}}{\hat{\tau}} [-\hat{p}(\hat{\tau})^3 + 3\hat{p}(\hat{\tau}) - 2\exp(-\hat{\tau})] \\ & + \frac{1}{12} \left(\frac{2\epsilon}{3}\right)^2 \int_0^\infty d\hat{\tau} (d\hat{p}/d\hat{\tau})^2. \end{aligned} \quad (6.17)$$

This expression has the virtue of being a local functional of $\hat{p}(\hat{\tau})$, so that the consequent stationarity condition will be a differential equation for $\hat{p}(\hat{\tau})$. Moreover, the (global) constraint that $p(\tau)$ be normalized to unity, $\int_0^\infty d\tau p(\tau) = 1$, is exchanged for the (local) boundary condition $\hat{p}(0) = 1$.

We now demand that \tilde{f}^{var} be stationary with respect to $\hat{p}(\hat{\tau})$, i.e. that $\delta\tilde{f}^{\text{var}}/\delta\hat{p}(\hat{\tau}) = 0$. The details of computing the functional derivative of \tilde{f}^{var} with respect to $\hat{p}(\hat{\tau})$ are deferred to Appendix H; what results is the stationarity condition, correct to $\mathcal{O}(\epsilon^4)$,

$$0 = \frac{\delta\tilde{f}^{\text{var}}}{\delta\hat{p}(\hat{\tau})} = -\left(\frac{2\epsilon}{3}\right)^3 \frac{1}{4\hat{\tau}} [1 - \hat{p}(\hat{\tau})] + \left(\frac{2\epsilon}{3}\right)^3 \frac{1}{4\hat{\tau}} [1 - \hat{p}(\hat{\tau})^2] - \left(\frac{2\epsilon}{3}\right)^2 \frac{1}{6} \frac{d^2\hat{p}}{d\hat{\tau}^2}, \quad (6.18)$$

or, equivalently,

$$\hat{\tau} \frac{d^2\hat{p}}{d\hat{\tau}^2} = \epsilon\hat{p}(\hat{\tau})[1 - \hat{p}(\hat{\tau})], \quad (6.19)$$

correct to $\mathcal{O}(\epsilon)$. Normalization of $p(\tau)$ leads to the boundary condition $\hat{p}(0) = 1$. As $p(\tau)$ does not contain a δ -function contribution at $\tau = 0$ (see [60]), \hat{p} obeys the additional boundary condition $\hat{p}(\infty) = 0$.

Before solving the stationarity condition we note that $p(\tau)$ depends parametrically on the crosslink density, so it would be more accurate to denote it by $p(\tau; \epsilon)$. We now introduce the scaling function $\pi(\theta)$ in terms of which $p(\tau; \epsilon)$ is given by $p(\tau; \epsilon) = (2/\epsilon)\pi(2\tau/\epsilon)$. In other words we transform the dependent and independent variables as follows:

$$\epsilon p(\tau; \epsilon)/2 = \pi(\theta), \quad (6.20 a)$$

$$\tau = \epsilon\theta/2. \quad (6.20 b)$$

In this way, up to an elementary factor, the dependence of $p(\tau; \epsilon)$ on τ and ϵ is combined into a dependence on a single scaling variable θ (see [61]). Then the Laplace transform of the scaling function $\hat{\pi}(\hat{\theta})$ is defined via

$$\hat{\pi}(\hat{\theta}) \equiv \int_0^{\infty} d\theta \pi(\theta) \exp(-\hat{\theta}\theta), \quad (6.21)$$

so that

$$\hat{p}(\hat{\tau}) = \hat{\pi}(\hat{\theta}) \quad (6.22 a)$$

$$\epsilon \hat{\tau} / 2 = \hat{\theta}. \quad (6.22 b)$$

In terms of $\hat{\pi}(\hat{\theta})$, and neglecting $\mathcal{O}(\epsilon)$ contributions, the stationarity condition then becomes

$$\hat{\theta} \frac{d^2 \hat{\pi}}{d\hat{\theta}^2} = 2\hat{\pi}(\hat{\theta})(1 - \hat{\pi}(\hat{\theta})), \quad (6.23)$$

subject to the boundary conditions $\hat{\pi}(0) = 1$ and $\hat{\pi}(\infty) = 0$.

We have been unable to solve this nonlinear ordinary differential equation for $\hat{\pi}(\hat{\theta})$ analytically. One might consider solving this differential equation numerically, and then inverting the solution numerically to obtain $\pi(\theta)$ and hence $p(\tau)$. Whilst this is possible in principle, the numerical inversion of Laplace transforms is notoriously unstable. Instead, we have found it preferable to take the inverse transform of the differential equation analytically, and thus we obtain the nonlinear integro-differential equation and constraint for $\pi(\theta)$,

$$\frac{\theta^2 d\pi}{2 d\theta} = (1 - \theta)\pi(\theta) - \int_0^{\theta} d\theta' \pi(\theta')\pi(\theta - \theta'), \quad (6.24 a)$$

$$\int_0^{\infty} d\theta \pi(\theta) = 1, \quad (6.24 b)$$

the constraint resulting from normalization.

We shall obtain $\pi(\theta)$ (and hence $\rho(\tau)$) in section 6.5, and discuss the consequences of the physical values of q and $p(\tau)$. Before doing so, we shall adopt a different point of view, in which we focus not on the variational extremization of the free energy but instead on the self-consistent equation for the order parameter.

6.4. Self-consistency condition for the order parameter

In section 6.3 we enforced the stationarity of the effective Hamiltonian only with respect to the parameters q and $p(\tau)$ of our order parameter hypothesis, and not with respect to arbitrary variations. As a consequence, we are not yet in a position to address whether or not the resulting order parameter is a true saddle point of the effective Hamiltonian. In the present subsection we establish that the solution that we have found is indeed a true saddle point of the effective Hamiltonian by directly analysing the stationarity conditions (6.3 a) and (6.3 b) themselves. We emphasize that this approach allows us to circumvent the difficulties discussed in section 2.6 that arise in the computation of the contribution to the free energy associated with changes in the indistinguishability factors introduced by the crosslinks. The results of this subsection have been briefly reported in [13].

We insert the hypothesis given in equations (6.7 a) and (6.7 b) into the stationarity

conditions (6.3 a) and (6.3 b), derived in section 6.1, to obtain

$$\begin{aligned}
 & (1-q)\delta_{\hat{q},\hat{0}} + q\delta_{\hat{q},\hat{0}} \int_0^\infty d\tau p(\tau) \exp(-\hat{q}^2/2\tau) \\
 & \left\langle \int_0^1 dt \exp(i\hat{q} \cdot \hat{c}(t)) \right. \\
 & \quad \times \exp \left\{ \mu^2 V^{-n} q \sum_{\hat{k}} \delta_{\hat{k},\hat{0}} \int_0^\infty d\tau p(\tau) \exp(-\hat{k}^2/2\tau) \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \Bigg\rangle_{n+1}^W \\
 & = \frac{\left\langle \int_0^1 dt \exp(i\hat{q} \cdot \hat{c}(t)) \right. \\
 & \quad \times \exp \left\{ \mu^2 V^{-n} q \sum_{\hat{k}} \delta_{\hat{k},\hat{0}} \int_0^\infty d\tau p(\tau) \exp(-\hat{k}^2/2\tau) \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \Bigg\rangle_{n+1}^W}{\left\langle \exp \left\{ \mu^2 V^{-n} q \sum_{\hat{k}} \delta_{\hat{k},\hat{0}} \int_0^\infty d\tau p(\tau) \exp(-\hat{k}^2/2\tau) \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \right\rangle_{n+1}^W}.
 \end{aligned} \tag{6.25}$$

Here, in both the numerator and the denominator we have relaxed the constraints on the summations having coefficient μ^2 by (i) doubling the range of the summations to include the entire higher-replica sector by making use of the property of the hypothesis $\Omega_{\hat{k}} = \Omega_{-\hat{k}}^*$, (ii) including the 1-replica sector terms (which vanish by the MTI of the order parameter hypothesis), and (iii) inserting identical factors associated with the 0-replica sector. It should be noted that equation (6.25) also follows from the direct application of the Weiss molecular-field method.

As shown at the end of Appendix I, evaluation of the numerator and denominator of the right-hand side yields

$$\begin{aligned}
 & (1-q)\delta_{\hat{q},\hat{0}} + q\delta_{\hat{q},\hat{0}} \int_0^\infty d\tau p(\tau) \exp(-\hat{q}^2/2\tau) \\
 & = \exp(-\mu^2 q)\delta_{\hat{q},\hat{0}} + \exp(-\mu^2 q)\delta_{\hat{q},\hat{0}} \int_0^\infty d\tau \exp(-\hat{q}^2/2\tau) \sum_{r=1}^\infty \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_{r+1} \\
 & \quad \times \int_0^\infty d\tau_1 \cdots d\tau_r p(\tau_1) \cdots p(\tau_r) \delta(\tau - \mathcal{I}^{(r)}), \tag{6.26 a}
 \end{aligned}$$

$$\frac{1}{\mathcal{I}^{(r)}} \equiv \frac{1}{\mathcal{W}^{(r)}} + \mathcal{S}_{r+1,r+1} - \frac{2}{\mathcal{W}^{(r)}} \sum_{\rho=1}^r \mathcal{U}_\rho^{(r)} \mathcal{S}_{\rho,r+1} - \sum_{\rho,\rho'=1}^r \mathcal{S}_{r+1,\rho} \mathcal{C}_{\rho\rho'}^{(r)} \mathcal{S}_{\rho',r+1}, \tag{6.26 b}$$

where the limit $n \rightarrow 0$ has been taken everywhere except in the dimension of \hat{q} , and where $\mathcal{S}_{\rho\rho'}$, $\mathcal{U}^{(r)}$, $\mathcal{W}^{(r)}$ and $\mathcal{C}^{(r)}$ are, respectively, defined in equations (B2), (F2 a), (F2 b) and (F2 c), and depend on $\{s_1, \dots, s_{r+1}\}$ and $\{\tau_1, \dots, \tau_{r+1}\}$. It should be emphasized that equation (6.26 a) is not solved by any sharp distribution of localization lengths $p(\tau) = \delta(\tau - \xi^{-2})$. Thus, a variational hypothesis involving a sharp distribution gives at best a variational approximation, whereas a variational hypothesis involving a non-sharp distribution has the potential to yield an exact saddle point, and we shall find such an exact saddle point below, at least in the vicinity of the vulcanization transition.

We now extract information about q and $p(\tau)$ from equation (6.26 a). First, we take the limit $\hat{q}^2 \rightarrow 0$, via a sequence for which $\hat{q} = \mathbf{0}$. In this limit, the left-hand side becomes q , and on the right side each integral gives a factor of unity, yielding the self-consistency condition for the gel fraction q ,

$$q = 1 - \exp(-\mu^2 q), \tag{6.27}$$

i.e. precisely the self-consistency condition for q found from the free energy approach in section 6.3 and discussed there.

Having decoupled the issue of the gel fraction q from the issue of the distribution $p(\tau)$ we now return to $p(\tau)$ itself. By considering equation (6.26 *b*) for a fixed non-zero value of \hat{q}^2 , and using Lerch's uniqueness theorem for Laplace transforms [62] we find that indeed the hypothesis solves the self-consistency condition for $\{\Omega_{\mathbf{k}}^\alpha, \Omega_{\mathbf{k}}^\beta\}$ provided that the distribution $p(\tau)$ satisfies the condition

$$qp(\tau) = \exp(-\mu^2 q) \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_{r+1} \int_0^\infty d\tau_1 \cdots d\tau_r p(\tau_1) \cdots p(\tau_r) \delta(\tau - \Upsilon_r). \quad (6.28)$$

This equation for $p(\tau)$ is, for all values of μ^2 , identically satisfied if $q = 0$.

We have not, thus far, made any approximations beyond that of mean field theory. In order to render equation (6.28) tractable, we now restrict our attention to the vicinity of the transition regime in the solid state, i.e. to values of ϵ , as defined in equation (6.11), satisfying $0 \leq \epsilon \ll 1$. This restriction allows us to assume that q is small, and that only localization lengths much larger than the free-macromolecule radius of gyration have an appreciable probability, i.e. $p(\tau)$ only gives appreciable weight for $0 < \tau \ll 1$. Thus, we need retain in equation (6.28) only terms for which r is 1 or 2, and may expand $\Upsilon^{(1)}$ to $\mathcal{O}(\tau^2)$ and $\Upsilon^{(2)}$ to $\mathcal{O}(\tau^1)$. As discussed in Appendix J, in terms of the scaling function $\pi(\theta)$ introduced in equation (6.20 *a*), we recover equation (6.24 *a*) subject to the normalization condition equation (6.24 *b*), i.e. precisely the stationarity condition for $p(\tau)$ found from the free-energy approach.

Thus, the condition that the order parameter be self-consistent turns out to be identical to the condition that the effective Hamiltonian be stationary with respect to variations within the subspace spanned by the hypothesized form of the order parameter. The form for the order parameter hypothesized in equation (3.14) is not merely a variational form but in fact gives an exact saddle point of the effective Hamiltonian, equation (5.12 *b*).

We have obtained the equation for the gel fraction q , equation (6.10), and the equations for the scaled distribution $\pi(\theta)$, equations (6.24 *a*) and (6.24 *b*), from two different points of view. In the previous subsection we have discussed the consequences of equation (6.10) for q . In the following subsection we shall discuss the solution of equations (6.24 *a*) and (6.24 *b*) for $\pi(\theta)$, and elaborate on the physical consequences of our results for q and $p(\tau)$.

6.5. Characteristics of the amorphous solid state

For the sake of completeness we first restate the results concerning the gel fraction q that were found in section 6.3 from the self-consistency condition on q , equation (6.10). For all values of μ^2 we find the solution $q = 0$, corresponding to the liquid state. For $\mu^2 > 1$ an additional solution appears, emerging continuously from $q = 0$ at $\mu^2 = 1$, and describing the equilibrium amorphous solid state, as shown in figure 1. For $\mu^2 \gg 1$, i.e. the highly crosslinked regime, q approaches unity asymptotically as $q \sim 1 - \exp(-\mu^2)$. In terms of the deviation of the crosslink density from criticality, i.e. ϵ defined in equation (6.11), the critical regime is $0 \leq \epsilon \ll 1$. In this regime we may solve perturbatively for q , obtaining $q = 2\epsilon/3 + \mathcal{O}(\epsilon^2)$, equation (6.12).

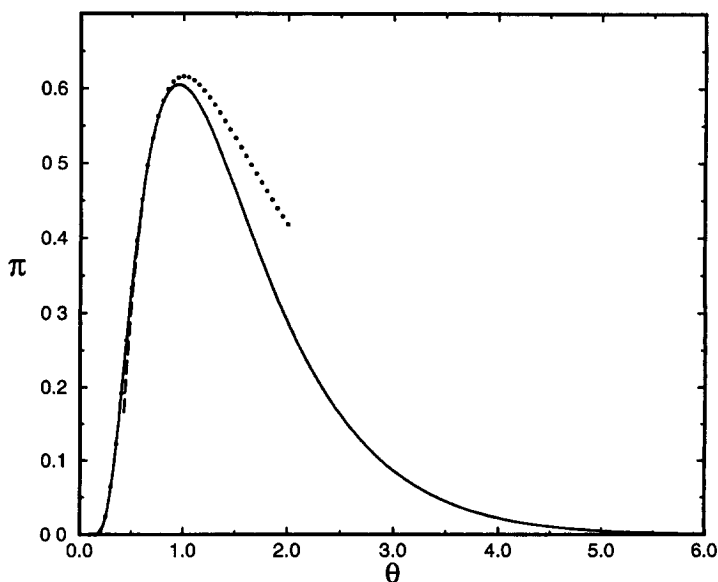


Figure 2. Scaling function $\pi(\theta)$ (full line) for the probability distribution of localization lengths; asymptotic form for $\theta \rightarrow 0$ (dotted line); asymptotic form for $\theta \rightarrow \infty$ (broken line).

It should be noted that the stationarity condition on q , equation (6.10), is precisely the condition obtained by Erdős and Rényi in the context of random graph theory [58], which can also be interpreted as a mean-field treatment of percolation. In particular, Erdős and Rényi showed that for a random graph of N points and $\mu^2 N/2$ edges the probability for the fraction of points in the largest component to differ from the solution q of equation (6.10) vanishes in the $N \rightarrow \infty$ limit. A related approach to the theory of macromolecular networks [34] has also led to equation (6.10). This is physically quite reasonable: one would anticipate that the transition from liquid to solid would occur when the density of crosslinks is sufficient to create a macroscopically extended network of crosslinked macromolecules.

We now address the distribution of localization lengths via the scaling form $\pi(\theta)$. We have solved both the integro-differential equation (6.24 *a*) and the differential equation (6.23) numerically [63, 64], and the solution of equation (6.24 *a*) is shown in figure 2. As we see in this figure, the scaling function $\pi(\theta)$ has a single maximum near $\theta = 1$, away from which it decays rapidly. In fact, states for which $\pi(\theta)$ takes negative values are not ruled out by the hypothesis, equation (3.14), but are not found as solutions of the stationarity condition, equations (6.24 *a*) and (6.24 *b*).

We are able to obtain asymptotic properties of $\pi(\theta)$ analytically. The asymptotic form $\pi(\theta) \sim a\theta^{-2} \exp(-2/\theta)$ (for $\theta \ll 1$) is obtained from equation (6.24 *a*) by neglecting the second term on the right-hand side. Notice the essential singularity at the origin: $\pi(\theta)$ vanishes very rapidly indeed as $\theta \rightarrow 0$. The coefficient $a \approx 4.554$ cannot be obtained from local asymptotic analysis. Instead we have obtained it separately by the numerical solution of equation (6.23), as discussed in [64]. The asymptotic form $\pi(\theta) \sim 3(b\theta - 3/5) \exp(-b\theta)$ (for $\theta \gg 1$) is obtained by computing the inverse Laplace transform of the approximate analytical solution of equation (6.23) near the point $\hat{\theta} = -b$, at which $\hat{\pi}(\hat{\theta})$ diverges. The coefficient $b \approx 1.678$ was obtained separately by determining the (negative) value of $\hat{\theta}$ at which the numerical

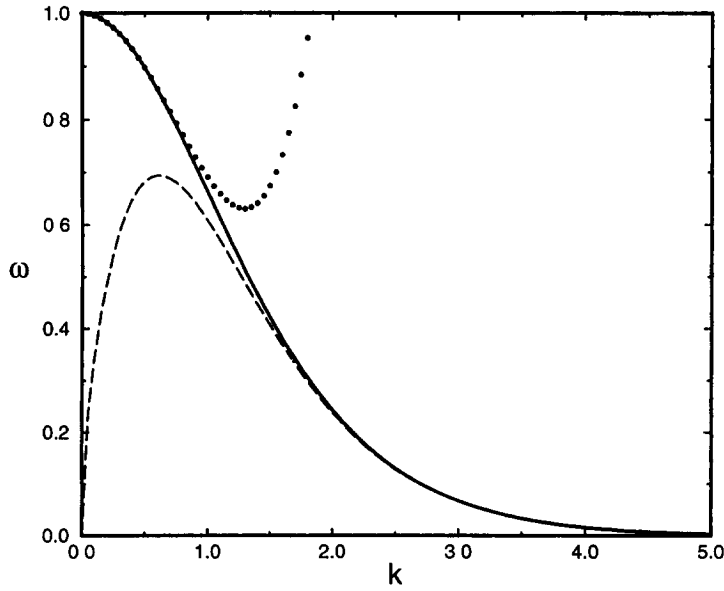


Figure 3. Scaling function $\omega(k)$ for the order parameter (full line); asymptotic form for $k \rightarrow 0$ (dotted line); asymptotic form for $k \rightarrow \infty$ (broken line).

solution of equation (6.23) diverges. Notice the exponential decay of $\pi(\theta)$ for large θ : $\pi(\theta)$ goes to zero quickly as $\theta \rightarrow \infty$. For the sake of comparison with the numerical results, the small- and large- θ asymptotic forms for $\pi(\theta)$ are also shown in figure 2. A distribution of localization lengths also features in Panyukov's approach to the well-crosslinked regime (see [52]).

In addition to providing the distribution of localization lengths, knowledge of $\pi(\theta)$ allows us to construct the order parameter $\Omega_{\hat{k}}$. By using equations (6.20 a) and (6.20 b) in equation (3.14) we obtain

$$\Omega_{\hat{k}} = (1 - 2\epsilon/3) \delta_{\hat{k},\hat{0}} + (2\epsilon/3) \delta_{\hat{k},\hat{0}} \omega((2\hat{k}^2/\epsilon)^{1/2}), \quad (6.29 a)$$

$$\omega(k) \equiv \int_0^\infty d\theta \pi(\theta) \exp(-k^2/2\theta). \quad (6.29 b)$$

Although we do not have an exact analytical expression for $\pi(\theta)$, we can compute $\omega(k)$ numerically. We do this by inserting the numerical values of $\pi(\theta)$ into equation (6.29 b), and show the result for $\omega(k)$ in figure 3. We are able to obtain analytical asymptotic expressions for $\omega(k)$. For $q \ll 1$ the result simply follows from expanding the exponential function in equation (6.29 b) in powers of q , thus obtaining

$$\omega(k) \sim 1 - \frac{k^2}{2} \int_0^\infty d\theta \theta^{-1} \pi(\theta) + \frac{k^4}{8} \int_0^\infty d\theta \theta^{-2} \pi(\theta) + \dots \quad (6.30 a)$$

$$= 1 - 0.4409q^2 + 0.1316q^4 + \dots, \quad \text{for } q \ll 1. \quad (6.30 b)$$

We see that $\omega(k)$ departs quadratically from its absolute maximum of unity at the

origin. For $k \gg 1$ one can replace $\pi(\theta)$ by its large- θ asymptotic form in equation (6.29 b) to obtain

$$\omega(k) \sim \left(\frac{9\pi k^3}{(8b)^{1/2}} \right)^{1/2} \exp(- (2bk^2)^{1/2}) \left(1 + \frac{27}{40(2bk^2)^{1/2}} + \dots \right), \quad \text{for } k \gg 1. \quad (6.30 c)$$

We see that $\omega(k)$ decays exponentially to zero for large k . For the sake of comparison with the numerical results, the small- and large- k asymptotic forms for $\omega(k)$ are also shown in figure 3.

To summarize, as shown in section 6.2, the liquid state of a system of randomly crosslinked macromolecules becomes unstable when the mean number of crosslinks per macromolecule $[M]/N$ is increased beyond a certain critical value M_c/N , corresponding to $\mu^2 = 1$. At this critical point the system exhibits a continuous phase transition from the liquid state to the amorphous solid state. As shown in sections 6.3 and 6.4, this solid state is characterized by a gel fraction q , which grows from a value of zero at the critical point with the classical exponent $\beta = 1$ (see [66]): $q \sim \epsilon \sim \mu^2 - 1 \sim ([M] - M_c)/N$. The amorphous solid state is further characterized by the statistical distribution of localization lengths $2\xi^{-3}p(\xi^{-2})$. In the vicinity of the transition the dependence of this distribution on the control parameter ϵ and the (inverse square) localization length τ is determined by a universal scaling function (of a single variable) $\pi(\theta)$, i.e. $p(\tau) = (2/\epsilon)\pi(2\tau/\epsilon)$. This universality guarantees that $\pi(\theta)$ need only be computed once for all near-critical crosslink densities. As already mentioned in the present subsection, $\pi(\theta)$ has a single maximum, away from which it decays rapidly. Hence, the fraction of localized monomers that are localized on length scales much larger than $\epsilon^{-1/2}$ is exceedingly small. Our result for $p(\tau)$ also predicts that the fraction of localized monomers with localization lengths much smaller than $\epsilon^{-1/2}$ is also exceedingly small. This provides an *a posteriori* confirmation of the internal consistency of the perturbation expansion in powers of ξ^{-2} upon which our results rely. However, the detailed form of the distribution for localization lengths much smaller than $\epsilon^{-1/2}$ (e.g. for localization lengths of the order of the radius of gyration of a free macromolecule) is unreliable because such localization lengths are not within the range of validity of the perturbation expansion. The rapid decay of $p(\tau)$ away from its maximum guarantees that its moments are finite. This character, together with the scaling form of $p(\tau)$ ensures that the moments scale in the following manner: $[\xi^{-2m}] \sim (([M] - M_c)/N)^{m+1}$. Furthermore, as the distribution has single maximum it is sensible to define a typical localization length ξ_{typ} associated with the most probable localization length. This length ξ_{typ} obeys the scaling relation $\xi_{\text{typ}} \sim (\mu^2 - 1)^{-1/2}$. Thus, a simple, reasonable approximation to the true distribution $p(\tau)$ would be a sharp distribution, e.g. $\delta(\tau - \epsilon/2)$.

We have seen in section 6.4 that the order parameter hypothesized in section 3.3 and determined in sections 6.3 and 6.4 is a solution of the stationarity condition for the free energy equation (6.3 b). This is in contrast with the hypothesis analysed in [12], in which it was assumed that $q = 1$ and $p(\xi^{-2}) = \delta(\xi^{-2} - \bar{\xi}^{-2})$ (i.e. that all monomers share a common localization length). The hypothesis of [12] does not satisfy the stationarity condition, and therefore only provides a variational bound on the free energy. That our result for the order parameter is a saddle point of the free energy, rather than merely a variational bound, is a feature of considerable significance. The consequent exact vanishing of the linear term in the expansion of the effective Hamiltonian, equation (5.12 b), in powers of the departure from the

known stationary value streamlines further analysis of, for example, linear stability, fluctuations, correlations, and response to perturbations [47].

6.6. Comparison with numerical simulations

Extensive numerical simulations of both macromolecular melts and well-crosslinked macromolecular networks have been performed by Grest and Kremer, and others; for a review see [67]. On the other hand, until the recent work of Barsky and Plischke [68], relatively little attention had been devoted to simulations of the regime in which the number of crosslinks is comparable to the number of macromolecules (i.e. the vicinity of the liquid-to-amorphous solid transition). It should be remarked that from the computational point of view this is a daunting regime. In their simulations, Barsky and Plischke observe a continuous transition from the liquid to the amorphous solid state, and extract a universal scaling function describing the distribution of localization lengths. Whilst their numerical results are in strong qualitative agreement with the analytical predictions described in the present article, thus providing support for the theoretical picture of amorphous solidification discussed here, there appear to be quantitative differences. At present, the precise origin of these differences is unclear: a possible source is the relatively short length of the macromolecules used in the simulations, for which mean-field theory is expected to require substantial fluctuation corrections over a moderately wide range of near-critical crosslink densities.

7. Incorporation of density-sector correlations

Until now we have entirely neglected fluctuations in the fields $\Omega_{\mathbf{k}}^{\alpha}$, $\Omega_{\hat{k}}$ and $\omega_{\mathbf{k}}$ in the computation of the functional integrals in the numerator and denominator of equation (5.11). Instead we have approximated the functional integrals by the stationary values of their integrands. This amounts to making a mean-field approximation, in which correlations between fluctuations of the fields are neglected.

As a consequence of this strategy, the excluded-volume interaction has played a subsidiary role: its presence has been required, in order to maintain the stability of the physical system with respect to the formation of macroscopically inhomogeneous states, e.g. via crystallization or collapse (which would be detected by their non-zero value of the order parameter in the 1-replica sector), even at crosslink densities large enough to destabilize the liquid state with respect to macroscopically translationally invariant states (i.e. equilibrium amorphous solids). However, having accomplished this by guaranteeing the stability of the 1-replica sector, the excluded-volume interaction has played no further role. Indeed, the precise value of the excluded-volume parameter λ does not even feature in the mean-field free energy of either the liquid state or the equilibrium amorphous solid state (in the same way that the exchange coupling constant of a magnetic system does not feature in the mean-field free energy of the paramagnetic state). Thus, amongst the correlations that we have entirely neglected are those between fluctuations of the density of the system, i.e. correlations between the 1-replica sector fields $\Omega_{\mathbf{k}}^{\alpha}$.

There are two reasons why we should seek to improve the theory by incorporating density–density correlations, at least at some level. (It should be pointed out that Ball and Edwards have undertaken the task of incorporating correlations in their approach to crosslinked macromolecular systems [6, 7].) First, at least at high densities, the resulting screening of the excluded-volume interaction gives an

accurate treatment of interaction effects [19]. Second, such correlations would reflect the statistical tendency for the macromolecules to avoid one another. This would have the effect of introducing a statistical preference for configurations in which macromolecules stay apart, and a barrier between topologically distinct configurations. Thus, one might imagine the following scenario. In a given realization of the supercritically crosslinked system without the correlations associated with self-avoidance there is no statistical bias against macromolecules passing through one another. Thus there is no apparent mechanism for creating distinct ways for the macromolecules to localize themselves, and the system would exhibit a single family of (translational- and rotational-symmetry-related) solid equilibrium states. If, on the other hand, correlations are incorporated, then there can be at least statistical barriers between symmetry-unrelated ways for the macromolecules to become localized, e.g. topologically distinct interweavings of the macromolecules. Thus, one might anticipate a situation in which the incorporation of correlations allows the system to exhibit symmetry-unrelated equilibrium states, a scenario that could be revealed through the mechanism of the spontaneous breakdown of the permutation symmetry amongst the replicas. Certain ideas in this direction have been explored in [31]. For a discussion of related issues in the context of spin glasses, see [33].

7.1. Free energy

We now set about the task of computing the quotient of functional integrals, equation (5.12a), with improved accuracy, in order to incorporate the effect of the excluded-volume interaction. With regard to the functional integral in the numerator our strategy will be to treat the 1-replica sector in the Gaussian approximation, resulting in an improved effective Hamiltonian for the higher-replica sector field $\Omega_{\hat{k}}$, which we then treat at the mean-field level. The functional integral in the denominator will also be treated in the Gaussian approximation. We assume that at the relevant saddle points of the improved effective Hamiltonian the order parameter $\Omega_{\hat{k}}$ will continue to have the property of being MTI, as described in section 3.1.

To implement this strategy, we expand \mathcal{F}_n , equation (5.12b), to quadratic order in the 1-replica sector field $\Omega_{\mathbf{k}}^{\alpha}$ for an arbitrary value of the higher-replica sector field $\Omega_{\hat{k}}$, except for the restriction that $\Omega_{\hat{k}}$ be MTI. Thus we obtain

$$\begin{aligned} nd\mathcal{F}_n(\{\Omega_{\mathbf{k}}^{\alpha}, \Omega_{\hat{k}}\}) \approx & \frac{\mu^2}{V^n} \sum_{\hat{k}} \dagger |\Omega_{\hat{k}}|^2 - \ln \left\langle \exp \left\{ \frac{2\mu^2}{V^n} \sum_{\hat{k}} \dagger \operatorname{Re} \Omega_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \right\rangle_{n+1}^W \\ & + \tilde{\lambda}_{n\nu}^2 \sum_{\alpha, \alpha'=0}^n \sum_{\mathbf{k}} \dagger (\delta^{\alpha, \alpha'} + \tilde{\lambda}_n^2(N/V) \mathcal{G}_{\mathbf{k}}^{\alpha\alpha'}) \Omega_{\mathbf{k}}^{\alpha} \Omega_{\mathbf{k}}^{\alpha'} + \mathcal{O}((\Omega_{\mathbf{k}}^{\alpha})^3), \end{aligned} \quad (7.1a)$$

$$\begin{aligned} \mathcal{G}_{\mathbf{q}}^{\alpha\alpha'} \equiv & \frac{\left\langle \int_0^1 dt \exp(i\mathbf{q} \cdot \mathbf{c}^{\alpha}(t)) \int_0^1 dt' \exp(-i\mathbf{q} \cdot \mathbf{c}^{\alpha'}(t')) \right. \\ & \left. \times \exp \left\{ 2\mu^2 V^{-n} \sum_{\hat{k}} \dagger \operatorname{Re} \Omega_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \right\rangle_{n+1}^W}{\left\langle \exp \left\{ 2\mu^2 V^{-n} \sum_{\hat{k}} \dagger \operatorname{Re} \Omega_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \right\rangle_{n+1}^W}, \end{aligned} \quad (7.1b)$$

in which $\nu \equiv N/V$ denotes the number of macromolecules per unit volume. Note that all terms linear in $\Omega_{\mathbf{k}}^\alpha$, as well as most terms that are quadratic in $\Omega_{\mathbf{k}}^\alpha$ vanish by virtue of the MTI property of $\Omega_{\hat{k}}$. The $\Omega_{\hat{k}}$ -dependent correlator $\mathcal{G}_q^{\alpha\alpha'}$ is discussed further, below, and is computed for a specific form of $\Omega_{\hat{k}}$ in Appendix K. Similarly, we expand \mathcal{F}^{den} , equation (5.12 c), to quadratic order in the field $\omega_{\mathbf{k}}$, obtaining

$$nd\mathcal{F}^{\text{den}}(\{\omega_{\mathbf{k}}\}) \approx \bar{\lambda}_0^2 \nu \sum_{\mathbf{k}}^\dagger (1 + \bar{\lambda}_0^2 \nu g_0(|\mathbf{k}|^2)) |\omega_{\mathbf{k}}|^2, \quad (7.2a)$$

$$g_0(|\mathbf{q}|^2) \equiv \left\langle \int_0^1 dt \exp(i\mathbf{q} \cdot \mathbf{c}(t)) \int_0^1 dt' \exp(-\mathbf{q} \cdot \mathbf{c}(t')) \right\rangle_1^{\text{W}}. \quad (7.2b)$$

The basic Debye correlator $g_0(|\mathbf{q}|^2)$ is computed in Appendix C. Next, we substitute the approximations to \mathcal{F}_n and \mathcal{F}^{den} , quadratic in $\Omega_{\mathbf{k}}^\alpha$ and $\omega_{\mathbf{k}}$ respectively, into equation (5.12 a), and perform the resulting Gaussian integrations over $\Omega_{\mathbf{k}}^\alpha$ and $\omega_{\mathbf{k}}$. These we do for each value of \mathbf{k} in the numerator and denominator, by noting the normalizations, equations (5.10 a) and (5.10 c), and applying the well-known result

$$\frac{\int \prod_{\alpha=0}^n d(\text{Re } z^\alpha) d(\text{Im } z^\alpha) \exp\left(-\sum_{\alpha,\alpha'=0}^n z^\alpha \mathcal{A}_1^{\alpha\alpha'} z^{\alpha'}\right)}{\int \prod_{\alpha=0}^n d(\text{Re } z^\alpha) d(\text{Im } z^\alpha) \exp\left(-\sum_{\alpha,\alpha'=0}^n z^\alpha \mathcal{A}_2^{\alpha\alpha'} z^{\alpha'}\right)} = \frac{\text{Det}_n \mathcal{A}_2}{\text{Det}_n \mathcal{A}_1}, \quad (7.3)$$

in which \mathcal{A}_1 and \mathcal{A}_2 are arbitrary Hermitian complex-valued $(n+1) \times (n+1)$ positive-definite matrices and Det_n denotes a (replica-space) determinant of an $(n+1) \times (n+1)$ matrix. Hence we obtain

$$\begin{aligned} \exp(-ndN\Phi_n(\mu^2, \{0\})) \approx \mathcal{B}_n \int \bar{\mathcal{D}}^\dagger \Omega \exp\left(-\frac{N\mu^2}{V^n} \sum_{\hat{k}}^\dagger |\Omega_{\hat{k}}|^2\right) \\ + N \ln \left\langle \exp\left\{\frac{2\mu^2}{V^n} \sum_{\hat{k}}^\dagger \text{Re } \Omega_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s))\right\}\right\rangle_{n+1}^{\text{W}} \\ \times \prod_{\mathbf{k}}^\dagger (1 + \bar{\lambda}_0^2 \nu g_0(|\mathbf{k}|^2)) / \prod_{\mathbf{k}}^\dagger \text{Det}_n (I_n + \bar{\lambda}_n^2 \nu \mathcal{G}_{\mathbf{k}}), \quad (7.4) \end{aligned}$$

where I_n is the $(n+1) \times (n+1)$ identity on the replica indices.

Now, our aim is to compute the free energy \tilde{f} , equation (2.13), and to do this we shall need the difference $\Phi_n(\mu^2, \{0\}) - \Phi_n(0, \{0\})$, as we see from equation (4.15). Thus, in addition to $\Phi_n(\mu^2, \{0\})$, which we have just obtained at the Gaussian level of approximation, we shall also need $\Phi_n(0, \{0\})$ at the Gaussian level of approximation. This can readily be obtained from equation (7.4) by setting μ^2 to zero throughout, except in the measure $\bar{\mathcal{D}}^\dagger \Omega$, equation (5.9 b), and in the coefficient of the quadratic term in the exponent: $-(N\mu^2/V^n) \sum_{\hat{k}}^\dagger |\Omega_{\hat{k}}|^2$. Then the logarithmic term vanishes, $\mathcal{G}_{\mathbf{k}}^{\alpha\alpha'}$ becomes $\delta^{\alpha\alpha'} g_0(|\mathbf{k}|^2)$, and $\bar{\lambda}_n^2$ becomes λ^2 , and the functional integration can be performed by using the normalization equation (5.9 b), all μ^2 -dependence cancelling from the result. Thus, we find

$$\exp[-ndN\Phi_n(0, \{0\})] \approx \exp(-n\lambda^2 N\nu/2) / \prod_{\mathbf{k}}^\dagger (1 + \lambda^2 \nu g_0(|\mathbf{k}|^2))^n. \quad (7.5)$$

By forming the difference $\Phi_n(\mu^2, \{0\}) - \Phi_n(0, \{0\})$ we thus arrive at the following expression for $[\tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)^n]$, in which 1-replica sector density fluctuations are incorporated at the Gaussian level, as indicated by the superscript gdf on \mathcal{F} :

$$[\tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)^n] \approx \int \mathcal{D}^\dagger \Omega \exp(-ndN \mathcal{F}_n^{\text{gdf}}(\{\Omega_{\hat{k}}\})), \quad (7.6 a)$$

$$\begin{aligned} nd \mathcal{F}_n^{\text{gdf}}(\{\Omega_{\hat{k}}\}) \equiv & \frac{\mu^2}{V^n} \sum_{\hat{k}}^\dagger |\Omega_{\hat{k}}|^2 - \ln \left\langle \exp \left\{ \frac{2\mu^2}{V^n} \sum_{\hat{k}}^\dagger \text{Re} \Omega_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \right\rangle_{n+1}^{\text{w}} \\ & + \frac{1}{\nu V} \sum_{\mathbf{k}}^\dagger \ln \text{Det}_n \left(\frac{I_n + \tilde{\lambda}_n^2 \nu \mathcal{G}_{\mathbf{k}}}{1 + \lambda^2 \nu g_0(|\mathbf{k}|^2)} \right) - \frac{1}{\nu V} \sum_{\mathbf{k}}^\dagger \ln \left(\frac{1 + \tilde{\lambda}_0^2 \nu g_0(|\mathbf{k}|^2)}{1 + \lambda^2 \nu g_0(|\mathbf{k}|^2)} \right). \end{aligned} \quad (7.6 b)$$

Following the same line of reasoning made in section 6.3, we shall now make a variational mean-field approximation for the remaining functional integral. To do this, we evaluate the effective Hamiltonian (7.6 b) using the hypothesis for $\Omega_{\hat{k}}$ given in equation (6.7 b). As was the case in section 6.3, this leads to an expression for the effective Hamiltonian in terms of q and $p(\tau)$, which we subsequently make stationary with respect to q and $p(\tau)$.

The next step in computing $[\tilde{Z}(\{i_e, s_e; i'_e, s'_e\}_{e=1}^M)^n]$ concerns the evaluation of the determinant on the replica indices, Det_n in equation (7.6 b). This can readily be accomplished provided we make the assumption that we only consider values of $\Omega_{\hat{k}}$ that are invariant under the permutation of replica indices (i.e. are replica symmetric). This is indeed the case for the form hypothesized in section 3.3. With this restriction, $\mathcal{G}_{\mathbf{k}}$ takes the form

$$\mathcal{G}_{\mathbf{k}}^{\alpha\alpha'} = \delta^{\alpha\alpha'} H_{\mathbf{k}} + (1 - \delta^{\alpha\alpha'}) h_{\mathbf{k}}, \quad (7.7)$$

which, for a given value of \mathbf{k} , has eigenvalues

$$H_{\mathbf{k}} + nh_{\mathbf{k}}, \quad \text{with degeneracy } 1, \quad (7.8 a)$$

$$H_{\mathbf{k}} - h_{\mathbf{k}}, \quad \text{with degeneracy } n, \quad (7.8 b)$$

so that $I_n + \tilde{\lambda}_n^2 \nu \mathcal{G}_{\mathbf{k}}$ has eigenvalues

$$1 + \tilde{\lambda}_n^2 \nu (H_{\mathbf{k}} + nh_{\mathbf{k}}), \quad \text{with degeneracy } 1, \quad (7.9 a)$$

$$1 + \tilde{\lambda}_n^2 \nu (H_{\mathbf{k}} - h_{\mathbf{k}}), \quad \text{with degeneracy } n. \quad (7.9 b)$$

Hence, we find that the determinant in equation (7.6 b) is given by

$$\text{Det}_n \left(\frac{I_n + \tilde{\lambda}_n^2 \nu \mathcal{G}_{\mathbf{k}}}{1 + \lambda^2 \nu g_0(|\mathbf{k}|^2)} \right) = \frac{(1 + \tilde{\lambda}_n^2 \nu (H_{\mathbf{k}} + nh_{\mathbf{k}}))(1 + \tilde{\lambda}_n^2 \nu (H_{\mathbf{k}} - h_{\mathbf{k}}))^n}{(1 + \lambda^2 \nu g_0(|\mathbf{k}|^2))^{n+1}}. \quad (7.10)$$

It should be noted that this expression has implicit dependence on n through $H_{\mathbf{k}}$, $h_{\mathbf{k}}$ and $\tilde{\lambda}_n^2$ but not through $g_0(|\mathbf{k}|^2)$.

Our next step involves making use of the fact that we shall ultimately be taking the replica limit, $n \rightarrow 0$. With this in mind, we make the expansions, valid for small n ,

$$H_{\mathbf{k}} = H_{\mathbf{k}}^{(0)} + nH_{\mathbf{k}}^{(1)} + \mathcal{O}(n^2), \quad (7.11 a)$$

$$h_{\mathbf{k}} = h_{\mathbf{k}}^{(0)} + nh_{\mathbf{k}}^{(1)} + \mathcal{O}(n^2), \quad (7.11 b)$$

$$\tilde{\lambda}_n^2 = \tilde{\lambda}_0^2 + n(\mu^2/\nu) \ln V + \mathcal{O}(n^2), \quad (7.11 c)$$

and note that $H_{\mathbf{k}}^{(0)} = g_0(|\mathbf{k}|^2)$ (as shown in Appendix K). By inserting these expansions into equation (7.10), taking the logarithm, and expanding for small n we obtain

$$\begin{aligned} \ln \text{Det}_n \left(\frac{I_n + \tilde{\lambda}_n^2 \nu \mathcal{G}_{\mathbf{k}}}{1 + \lambda^2 \nu g_0(|\mathbf{k}|^2)} \right) - \ln \left(\frac{1 + \tilde{\lambda}_0^2 \nu g_0(|\mathbf{k}|^2)}{1 + \lambda^2 \nu g_0(|\mathbf{k}|^2)} \right) \\ = n \left(\frac{\nu \tilde{\lambda}_0^2 (h_{\mathbf{k}}^{(0)} + H_{\mathbf{k}}^{(1)}) + \mu^2 H_{\mathbf{k}}^{(0)} \ln V}{1 + \tilde{\lambda}_0^2 \nu H_{\mathbf{k}}^{(0)}} \right) + n \ln \left(\frac{1 + \tilde{\lambda}_0^2 \nu (H_{\mathbf{k}}^{(0)} - h_{\mathbf{k}}^{(0)})}{1 + \lambda^2 \nu g_0(|\mathbf{k}|^2)} \right) + \mathcal{O}(n^2). \end{aligned} \quad (7.12)$$

Next, we insert equation (7.12) into equation (7.6 b), thus obtaining

$$\begin{aligned} nd \mathcal{F}_n^{\text{gdf}}(\{\Omega_{\hat{k}}\}) \approx \frac{1}{2} n \mu^2 \ln V + \frac{\mu^2}{V^n} \sum_{\hat{k}} \dagger |\Omega_{\hat{k}}|^2 \\ - \ln \left\langle \exp \left\{ \frac{2\mu^2}{V^n} \sum_{\hat{k}} \dagger \text{Re} \Omega_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \right\rangle_{n+1}^{\text{w}} \\ + \frac{n}{\nu V} \sum_{\mathbf{k}} \dagger \left(\frac{\nu \tilde{\lambda}_0^2 (h_{\mathbf{k}}^{(0)} + H_{\mathbf{k}}^{(1)}) + \mu^2 g_0(|\mathbf{k}|^2) \ln V}{1 + \tilde{\lambda}_0^2 \nu g_0(|\mathbf{k}|^2)} \right) \\ + \frac{n}{\nu V} \sum_{\mathbf{k}} \dagger \ln \left\{ \frac{1 + \tilde{\lambda}_0^2 \nu (g_0(|\mathbf{k}|^2) - h_{\mathbf{k}}^{(0)})}{1 + \lambda^2 \nu g_0(|\mathbf{k}|^2)} \right\} + \mathcal{O}(n^2), \end{aligned} \quad (7.13)$$

which is to be made stationary with respect to $\Omega_{\hat{k}}$ of the form (6.7 b) on which $\mathcal{F}_n^{\text{gdf}}$ depends both explicitly, and also implicitly, through $h_{\mathbf{k}}^{(0)}$ and $H_{\mathbf{k}}^{(1)}$. It should be noted that in obtaining this expression for $\mathcal{F}_n^{\text{gdf}}(\{\Omega_{\hat{k}}\})$ we have made use of the result, established in Appendix K, that $H_{\mathbf{k}}^{(0)} = g_0(|\mathbf{k}|^2)$, without which the limit $n \rightarrow 0$ would not exist.

We now evaluate $\mathcal{F}_n^{\text{gdf}}(\{\Omega_{\hat{k}}\})$ for $\Omega_{\hat{k}}$ given by equation (6.7 b). The second and third contributions to the right side of equation (7.13) are mean-field contributions, which have already been discussed in section 6, and which are computed in Appendix D. The fourth and fifth contributions are fluctuation corrections, resulting from the incorporation of 1-replica sector density fluctuations: it is upon these that we now focus. By reorganizing equation (7.13) and omitting contributions that are independent of both the gel fraction q and the distribution $p(\tau)$ we obtain

$$\tilde{f}^{\text{gdf}}\{q, p\} \equiv \lim_{n \rightarrow 0} \mathcal{F}_n^{\text{gdf}}(\{\Omega_{\hat{k}}\}) \quad (7.14 a)$$

$$\begin{aligned} = \tilde{f}^{\text{var}}\{q, p\} + \frac{1}{d\nu V} \sum_{\mathbf{k}} \dagger \frac{H_{\mathbf{k}}^{(1)}}{1 + \sigma_0 g_0(|\mathbf{k}|^2)} + \frac{\sigma_0}{d\nu V} \sum_{\mathbf{k}} \dagger \frac{h_{\mathbf{k}}^{(0)}}{1 + \sigma_0 g_0(|\mathbf{k}|^2)} \\ + \frac{1}{d\nu V} \sum_{\mathbf{k}} \dagger \ln \left[1 - \frac{\sigma_0 h_{\mathbf{k}}^{(0)}}{1 + \sigma_0 g_0(|\mathbf{k}|^2)} \right], \end{aligned} \quad (7.14 b)$$

where $\sigma_0 \equiv \bar{\lambda}_0^2 N/V \equiv \bar{\lambda}_0^2 \nu$. next, we recall that from equation (6.10) we know that q is small in the vicinity of the transition. This, together with the observation that terms for which $\mathbf{k} = \mathbf{0}$ are to be omitted from the fluctuation contributions, and that $h_{\mathbf{k}}^{(0)} \sim q$ (from equation (K 6) of Appendix K), shows that we may expand the last term in equation (7.14 b) as a power series in $h_{\mathbf{k}}^{(0)}$, which yields

$$\begin{aligned} \bar{f}^{\text{gdf}}\{q, p\} = \bar{f}^{\text{var}}\{q, p\} + \frac{1}{d\nu V} \sum_{\mathbf{k}} \dagger \frac{H_{\mathbf{k}}^{(1)}}{1 + \sigma_0 g_0(|\mathbf{k}|^2)} - \frac{1}{2 d\nu V} \sum_{\mathbf{k}} \dagger \left(\frac{\sigma_0 h_{\mathbf{k}}^{(0)}}{1 + \sigma_0 g_0(|\mathbf{k}|^2)} \right)^2 \\ - \frac{1}{3 d\nu V} \sum_{\mathbf{k}} \dagger \left(\frac{\sigma_0 h_{\mathbf{k}}^{(0)}}{1 + \sigma_0 g_0(|\mathbf{k}|^2)} \right)^3 + \mathcal{O}(q^4). \end{aligned} \quad (7.15)$$

We now examine the fluctuation corrections in equation (7.15) in detail. Equation (K 6) shows that $h_{\mathbf{k}}^{(0)}$ contains factors of the form $\exp(-k^2/\tau)$. For localization length distributions $p(\tau)$ that give appreciable weight only to $\tau \sim \epsilon$, we can assert that, where present, such factors effectively eliminate contributions from wave vectors larger in magnitude than $\sqrt{\epsilon}$. Thus, the two terms in equation (7.15) that involve $h_{\mathbf{k}}^{(0)}$ respectively scale with ϵ in d dimensions as $\epsilon^{2+d/2}$ and $\epsilon^{3+d/2}$, and thus are negligible for $d > 2$ and $d > 0$, respectively. On the other hand, $H_{\mathbf{k}}^{(1)}$ contains no such factors. In fact, the factorization of $H_{\mathbf{k}}^{(1)}$ into τ - and \mathbf{k} -dependent pieces exhibited in equation (K 5) enables us to identify the contribution to equation (7.15) associated with $H_{\mathbf{k}}^{(1)}$ as a renormalization of the coefficient of one particular term in $\bar{f}^{\text{var}}\{q, p\}$, namely

$$\frac{1}{12} \mu^4 q^2 \left\{ \frac{\tau_1 \tau_2}{\tau_1 + \tau_2} \right\}_{\tau} \rightarrow (1 + \mathcal{E}) \frac{1}{12} \mu^4 q^2 \left\{ \frac{\tau_1 \tau_2}{\tau_1 + \tau_2} \right\}_{\tau}, \quad (7.16 a)$$

where the renormalization parameter \mathcal{E} is given by

$$\mathcal{E} \equiv \frac{6\sigma_0}{d\nu V} \sum_{\mathbf{k}} \dagger k^2 \frac{g_1(|\mathbf{k}|^2) - g_2(|\mathbf{k}|^2)}{1 + \sigma_0 g_0(|\mathbf{k}|^2)}. \quad (7.16 b)$$

Now, in Appendix C, the functions $g_0(|\mathbf{k}|^2)$, $g_1(|\mathbf{k}|^2)$ and $g_2(|\mathbf{k}|^2)$ are computed. From the asymptotic properties of these functions we find that the renormalization of the coefficient \mathcal{E} is finite for $-2 < d < 4$, it being infrared divergent for $d < -2$ and ultraviolet divergent for $d > 4$. Thus, we find that in the physically relevant three-dimensional case the 1-replica-sector Gaussian density fluctuations simply give a finite renormalization of a coefficient in the variational free energy.

This renormalization has no effect on the behaviour of q as a function of μ^2 , which undergoes precisely the transition at $\mu^2 = 1$ that it undergoes at the mean-field level. Moreover, the only effect of this renormalization on $p(\tau)$ as a function of μ^2 , in the vicinity of the transition at $\mu^2 = 1$, is the finite rescaling: $p(\tau) = (2/\epsilon)\pi(2\tau/\epsilon) \rightarrow (2/\epsilon')\pi(2\tau/\epsilon')$, where $\epsilon' \equiv \epsilon/(1 + \mathcal{E})$. However, it must also be recognized that the relationship between the control parameter μ^2 and the mean number of crosslinks per macromolecule $[M]$ is modified by the fluctuation corrections. Thus, once the typical localization length is rescaled, the properties of the system are as found in section 6.5. Note, however, that although the location of the transition as measured by μ^2 is unaltered, the relationship between μ^2 and $[M]/N$ is changed by the incorporation of fluctuations; therefore, the location of the transition as measured by $[M]$ is altered.

8. Concluding remarks

As Charles Goodyear discovered in 1839 [69], the introduction of a sufficient density of permanent, random crosslinks causes a macromolecular liquid to be transformed into an amorphous solid, in which a non-zero fraction of macromolecules have spontaneously become localized. This system is a disordered system, in the sense that it comprises both thermally equilibrating as well as quenched random variables (i.e. the crosslink locations). In the present article we have presented a theoretical description of the physical properties of systems of macromolecules that have been randomly crosslinked. Our focus has been on the equilibrium properties of such systems, especially in the regime of the vulcanization transition.

The qualitative picture of randomly crosslinked macromolecular systems that emerges has the following primary features. For sufficiently few crosslinks, the equilibrium state of the system is liquid, thermal fluctuations causing all macromolecules to wander throughout the entire container given sufficient time (i.e. all macromolecules are delocalized). For sufficiently many crosslinks, the equilibrium state of the system is an amorphous solid state. In this state a non-zero fraction of macromolecules are self-consistently localized, exhibiting thermal fluctuations in location only over a certain distance scale, which we refer to as a localization length and which varies randomly from monomer to monomer. At a critical density of crosslinks, of order one per macromolecule, there is a continuous thermodynamic phase transition from the liquid state to the equilibrium amorphous solid state. The amorphous solid state is most unusual: the mean positions of the localized monomers are homogeneously random, exhibiting no periodicity whatsoever. The state is characterized by the fraction of monomers that are localized, together with the statistical distribution of their localization lengths. The symmetry properties of the amorphous solid state are striking. Microscopically, the amorphous solid state is one in which translational symmetry is spontaneously broken, certain monomers becoming localized about fixed mean positions, in contrast with the liquid state. Macroscopically, however, the amorphous solid state retains the translational symmetry of the liquid state, owing to the homogeneous randomness of the mean positions of the localized monomers. (Technically, this shows up as the macroscopic translational invariance of the value of the order parameter in the amorphous solid state.) This state bears the same relationship to the liquid and crystalline states as the spin glass state of certain magnetic systems bears to the paramagnetic and ferromagnetic states, in the following sense: the local static density fluctuations in the amorphous solid state correspond to local static magnetization fluctuations in the spin glass state. In both cases these fluctuations vanish, if averaged over the entire sample, and hence cannot serve as a global order parameter. Thus, moments of the static fluctuations higher than the first must be considered. In fully connected long-range spin glasses the distribution of these static fluctuations is Gaussian (in the replica symmetric theory), so that the second moment—the Edwards—Anderson order parameter—characterizes the state of the system completely. In contrast, in the amorphous solid state under consideration here, we find that all moments are equally important. Such non-Gaussian statistics are also encountered in strongly diluted long-range spin glasses [48], which show a percolation transition as described by equation (6.10).

To construct our picture of their physical properties, we have developed a field-theoretic representation of the statistical mechanics of randomly crosslinked

macromolecular systems. The order parameter capable of distinguishing between the various candidate states (liquid, amorphous, crystalline solid and globular) naturally emerges from this representation. The presence of quenched as well as annealed variables has been addressed by invoking the replica technique. We have derived the saddle-point equation from the effective Hamiltonian of this field-theoretic representation, this equation being equivalent to the self-consistent mean-field equation satisfied by the order parameter. Whilst it is not apparent how one might obtain the most general solution for the order parameter, we have proposed a physically motivated form for it, which allows for the possibilities of a liquid state and an amorphous solid state. This form is parametrized by the fraction of localized monomers, together with the statistical distribution of localization lengths. In fact, this form turns out to yield an exact solution of the saddle-point equation. It should be noted that we are only able to proceed with the calculation in the vicinity of the amorphous solidification transition, where the typical localization length is substantially larger than the radius of gyration of an isolated non-self-interacting macromolecule. In a refinement of this approach, we have incorporated a certain physically relevant class of correlations, associated with macromolecular repulsion, at the Gaussian level of approximation. No qualitative changes in our results stem from this refinement.

The quantitative picture of randomly crosslinked macromolecular systems that emerges from our field-theoretic representation has the following primary elements. At the mean-field level of approximation there is, for any crosslink density, a saddle point of the effective Hamiltonian that corresponds to the liquid state. However, for crosslink densities greater than a certain critical value, this liquid state is unstable. At this critical crosslink density a new saddle point of the effective Hamiltonian bifurcates continuously from the liquid-state saddle point. This new saddle point, which is characterized by a non-zero gel fraction and a specific distribution of localization lengths, corresponds to the amorphous solid state. The transition between the liquid and amorphous solid states is therefore continuous: in particular, the gel fraction and the inverse square of the typical localization length both increase from zero linearly with the excess of the crosslink density from its critical value. Moreover, the entire distribution of (inverse-square) localization lengths has a scaling form determined by a universal function of a single variable (which only need be computed once for all near-critical crosslink densities). Detailed results for the gel fraction and the distribution of localization lengths have been given. Thus, we see that what emerges is a quantitative picture of the amorphous solid state that confirms the qualitative picture proposed roughly a decade ago.

There are several other contexts in which one can make use of the circle of ideas that we have been using to explore the physical properties of randomly crosslinked macromolecular systems. First, one can apply them to a wide class of random-network-forming systems. Indeed, a straightforward extension [29] of the present work yields a theory of randomly crosslinked manifolds (i.e. higher-dimensional analogues of linear macromolecules [71, 72]). Similarly, one can address macromolecular networks formed via a random *endlinking* (rather than crosslinking) process, in which one end from each of several randomly selected macromolecules are linked to one other [73]. One can also consider networks formed via the (freely-jointed) endlinking of rigid or semi-flexible rods [73], subjects that are of particular relevance to certain biological structures.

This circle of ideas has also been used to develop a statistical-mechanical theory of continuous random (atomic or molecular) networks, and thus to develop a view of the structural glass transition [70]. In this case, what emerges is a picture of glass formation in which atomic or molecular units are (permanently chemically) bonded together at random, so as to develop an infinite network. Not only do the translational freedoms of the units become localized but so also do the orientational freedoms.

A particularly interesting problem arises in the context of NMR data on protein folding. The basic question is this: how much phase space is reduced due to a given number of constraints on the relative positions of certain monomer pairs [74]? We also mention the formal analogy between such questions and Gardner-type calculations in the field of neural networks [75]. Here, again, the basic issue is the reduction of phase space by quenched random constraints, even the distribution of randomness being generated in close analogy with the Deam–Edwards distribution, which leads to the same formal construction of $(n + 1)$ -fold replicated systems.

Finally, we raise the fascinating and difficult issue of the dynamical properties of randomly crosslinked macromolecular systems. In particular, it would be interesting to develop a semi-microscopic theory of the viscosity of the liquid state, and its divergence at the onset of solidification, as well as of the dynamics of the solid state itself. Our semi-microscopic approach is well suited to the application of the dynamical Lagrangian methods [76] that have been developed to address the dynamics of spin glasses [77].

Acknowledgments

It is a pleasure for us to thank Nigel Goldenfeld and Grzegorz Szamel for many stimulating and useful conversations. We gratefully acknowledge support from the US National Science Foundation through grants DMR91-57018 (P. M. G., H. E. C.), and DMR94-24511 (P. M. G., H. E. C.), from NATO through Collaborative Research Grant 940909 (P. M. G., A. Z.), and from the Deutsche Forschungsgemeinschaft through the Sonderforschungsbereich 345 (A. Z.). H. E. C. gratefully acknowledges support from a Graduate Fellowship at the University of Illinois at Urbana-Champaign. P. M. G. thanks for its hospitality the Institut für Theoretische Physik at Georg August Universität, Göttingen, where parts of the work reported here were undertaken. A. Z. thanks for its hospitality the Department of Physics at the University of Illinois at Urbana-Champaign where other parts of the work reported here were undertaken. P. M. G. wishes to use this occasion to record his sincere gratitude to Sir Sam Edwards, Phil Pincus and David Sherrington for the crucial opportunities that they have graciously provided for him.

Appendix A. Replica representation of disorder-averaged observables

In this Appendix we demonstrate how to evaluate the disorder average of products of equilibrium expectation values by using the replica technique. This complements the demonstration, given in section 4.2, of the connection between the disorder-averaged free energy \tilde{f} and the replica-Helmholtz free energy Φ_n .

Consider the disorder average of the product of g equilibrium expectation values of physical observables, i.e. $[\langle \mathcal{O}_1 \rangle_\chi \cdots \langle \mathcal{O}_g \rangle_\chi]$ (the meaning of the expectation value $\langle \cdots \rangle_\chi$ is discussed in section 3.1, immediately after equation (3.1)). In terms of sums

over disorder realizations and microscopic configurations this quantity is given by

$$[\langle \mathcal{O}_1 \rangle_\chi \cdots \langle \mathcal{O}_g \rangle_\chi] = \left[\frac{\sigma(\chi)^{-1} \text{tr}_1 \exp(-H_1) \Delta_1(\chi) \mathcal{O}_1 \cdots \sigma(\chi)^{-1} \text{tr}_g \exp(-H_g) \Delta_g(\chi) \mathcal{O}_g}{\sigma(\chi)^{-1} \text{tr}_1 \exp(-H_1) \Delta_1(\chi) \cdots \sigma(\chi)^{-1} \text{tr}_g \exp(-H_g) \Delta_g(\chi)} \right]. \quad (\text{A } 1)$$

Here, tr_1 denotes the trace (i.e. sum) over the configurations of one copy (or replica) of the system, without regard for distinguishability (i.e. without dividing by any symmetry factor), and tr_2 denotes a similar trace over another copy, etc. The factor $\sigma(\chi)$ ($\equiv \prod_a \nu_a!$) denotes the exact indistinguishability factor appropriate for the specific realization of the disorder and, accordingly, takes on values between $N!$ and unity. $\Delta_1(\chi)$ implements the constraints on the first copy of the system, being a factor that is unity for configurations of the first copy that satisfy the constraints χ , and zero otherwise. $\Delta_2(\chi)$ indicates a similar factor for the second copy, etc. The factor $\exp(-H_1)$ indicates the weight for configurations of the first copy, and similarly the factor $\exp(-H_2)$ indicates the weight for the second copy, etc. We now introduce a further $(n-g)$ factors $\sigma(\chi)^{-1} \text{tr} \exp(-H) \Delta(\chi)$ in both the numerator and denominator, which gives

$$[\langle \mathcal{O}_1 \rangle_\chi \cdots \langle \mathcal{O}_g \rangle_\chi] = \left[\frac{\sigma(\chi)^{-1} \text{tr}_1 \exp(-H_1) \Delta_1(\chi) \mathcal{O}_1 \cdots \sigma(\chi)^{-1} \text{tr}_g \exp(-H_g) \Delta_g(\chi) \mathcal{O}_g \times \sigma(\chi)^{-1} \text{tr}_{g+1} \exp(-H_{g+1}) \Delta_{g+1}(\chi) \cdots \sigma(\chi)^{-1} \text{tr}_n \exp(-H_n) \Delta_n(\chi)}{\sigma(\chi)^{-1} \text{tr}_1 \exp(-H_1) \Delta_1(\chi) \cdots \sigma(\chi)^{-1} \text{tr}_n \exp(-H_n) \Delta_n(\chi)} \right]. \quad (\text{A } 2)$$

In principle, this quantity is defined only for integral $n \geq g$, for which values of n it is constant. However, in the replica approach we regard n as a continuous variable, and formally determine this constant value by computing its limit as $n \rightarrow 0$. Thus, we obtain

$$\begin{aligned} & [\langle \mathcal{O}_1 \rangle_\chi \cdots \langle \mathcal{O}_g \rangle_\chi] \\ &= \lim_{n \rightarrow 0} [\text{tr}_1 \exp(-H_1) \Delta_1(\chi) \mathcal{O}_1 \cdots \text{tr}_g \exp(-H_g) \Delta_g(\chi) \mathcal{O}_g \text{tr}_{g+1} \exp(-H_{g+1}) \Delta_{g+1}(\chi) \\ & \quad \cdots \text{tr}_n \exp(-H_n) \Delta_n(\chi)], \quad (\text{A } 3) \end{aligned}$$

where we have used the fact that $\lim_{n \rightarrow 0} [\text{tr} \exp(-H) \Delta(\chi)]^n = 1$. As we have seen in section 2.5, in the context of macromolecular networks the disorder distribution is generated by the partition function itself, which is represented via the inclusion of an additional replica. In fact, it turns out that the naturally emerging order parameter involves the expectation value of variables associated with this additional replica, as we see in section 3. Such expectation values may be regarded as introducing additional χ -dependent factors into our disorder averages, e.g.

$$\begin{aligned} & [\Theta(\chi) \langle \mathcal{O}_1 \rangle_\chi \cdots \langle \mathcal{O}_g \rangle_\chi] \\ &= \lim_{n \rightarrow 0} [\Theta(\chi) \text{tr}_1 \exp(-H_1) \Delta_1(\chi) \mathcal{O}_1 \cdots \text{tr}_g \exp(-H_g) \Delta_g(\chi) \mathcal{O}_g \text{tr}_{g+1} \exp(-H_{g+1}) \Delta_{g+1}(\chi) \\ & \quad \cdots \text{tr}_n \exp(-H_n) \Delta_n(\chi)]. \quad (\text{A } 4) \end{aligned}$$

By using equation (A 4) and the Deam–Edwards distribution, equation (2.12), in a manner analogous to that used in the context of the free energy in section 4.2, we

In terms of the Wiener measure, the correlator is given, up to normalization, by

$$\left\langle \exp \left(-i \sum_{\rho=1}^r \mathbf{k}_\rho \cdot \mathbf{c}(s_\rho) \right) \right\rangle_1^W \propto \int \mathcal{D}\mathbf{c} \exp \left(-\frac{1}{2} \int_0^1 ds |\dot{\mathbf{c}}(s)|^2 \right) \exp \left(-i \sum_{\rho=1}^r \mathbf{k}_\rho \cdot \mathbf{c}(s_\rho) \right), \quad (\text{B } 3)$$

where the overdot denotes a derivative with respect to s . We express the configuration of the macromolecule in terms of the position of the end at $s = 0$, together with the tangent vector $\dot{\mathbf{c}}(s)$ via $\mathbf{c}(s) = \mathbf{c}(0) + \int_0^s ds' \dot{\mathbf{c}}(s') \theta(s - s')$, where $\theta(s)$ is the Heaviside θ -function. Then the measure $\mathcal{D}\mathbf{c}$ given by $\mathcal{D}\dot{\mathbf{c}} d\mathbf{c}(0)$, and the correlator becomes proportional to

$$\int d\mathbf{c}(0) \exp \left(-i \mathbf{c}(0) \cdot \sum_{\rho=1}^r \mathbf{k}_\rho \right) \int \mathcal{D}\dot{\mathbf{c}} \exp \left(-\frac{1}{2} \int_0^1 ds |\dot{\mathbf{c}}(s)|^2 \right) \times \exp \left(-i \int_0^1 ds \dot{\mathbf{c}}(s) \cdot \sum_{\rho=1}^r \mathbf{k}_\rho \theta(s_\rho - s) \right). \quad (\text{B } 4)$$

By performing the integral over $\mathbf{c}(0)$ we obtain the Kronecker δ -function factor $\delta_{0, \sum_{\rho=1}^r \mathbf{k}_\rho}^{(d)}$. By performing the integrals over the tangent vectors $\dot{\mathbf{c}}(s)$ we obtain the Gaussian factor

$$\exp \left(-\frac{1}{2} \sum_{\rho, \rho'=1}^r \mathbf{k}_\rho \cdot \mathbf{k}_{\rho'} \int_0^1 ds ds' \theta(s_\rho - s) \theta(s_{\rho'} - s') \delta(s - s') \right). \quad (\text{B } 5)$$

By performing the arclength integrals, and by setting to zero the wave vectors $\{\mathbf{k}_\rho\}_{\rho=1}^r$ in order to establish the correct normalization factor, we obtain the Wiener measure correlator equation (B 1). It should be noted that because $\min(s_\rho, s_{\rho'}) = \frac{1}{2}(s_\rho + s_{\rho'}) - \frac{1}{2}|s_\rho - s_{\rho'}|$, and because of the Kronecker δ -function factor, the exponent of the Wiener measure correlator can also be expressed as $\sum_{\rho, \rho'=1}^r \mathbf{k}_\rho \cdot \mathbf{k}_{\rho'} |s_\rho - s_{\rho'}|/4$.

Appendix C. Debye function and related functions

In this Appendix we give the basic Debye function $g_0(|\mathbf{k}|^2)$, as well as the two related functions $g_1(|\mathbf{k}|^2)$ and $g_2(|\mathbf{k}|^2)$. The Debye function $g_0(|\mathbf{k}|^2)$ is defined as the integral over arclength variables of the Wiener correlator equation (B 1) for the case $r = 2$ and $-\mathbf{k}_1 = \mathbf{k}_2 = \mathbf{k}$:

$$g_0(|\mathbf{k}|^2) \equiv \int_0^1 ds_1 ds_2 \langle \exp \{i\mathbf{k} \cdot (\mathbf{c}(s_1) - \mathbf{c}(s_2))\} \rangle_1^W = \int_0^1 ds_1 ds_2 \exp(-k^2 |s_1 - s_2|/2) \\ = \frac{\exp(-k^2/2) - (1 - \frac{1}{2}k^2)}{\frac{1}{2}(\frac{1}{2}k^2)^2} \sim \begin{cases} 1 - k^2/6, & \text{if } k^2 \ll 1, \\ 4/k^2, & \text{if } k^2 \gg 1. \end{cases} \quad (\text{C } 1)$$

The function $g_1(|\mathbf{k}|^2)$ is defined as

$$g_1(|\mathbf{k}|^2) \equiv \int_0^1 ds_1 ds_2 ds_3 \exp(-k^2 |s_1 - s_2|/2) (-\mathcal{S}_{1,3} + \mathcal{S}_{2,3})^2 \sim \begin{cases} 1/15, & \text{if } k^2 \ll 1, \\ 16/k^6, & \text{if } k^2 \gg 1. \end{cases} \quad (\text{C } 2)$$

The function $g_2(|\mathbf{k}|^2)$ is defined as

$$g_2(|\mathbf{k}|^2) \equiv \int_0^1 ds_1 ds_2 ds_3 \exp(-k^2|s_1 - s_2|/2)(-\mathcal{L}_{1,3} + \mathcal{L}_{2,3})(-\mathcal{L}_{1,4} + \mathcal{L}_{2,4})$$

$$\sim \begin{cases} 2/45, & \text{if } k^2 \ll 1, \\ 32/3k^6, & \text{if } k^2 \gg 1. \end{cases} \quad (\text{C } 3)$$

In $d = 3$ the relevant correction due to Gaussian density fluctuations involves the quantity $g_1(|\mathbf{k}|^2) - g_2(|\mathbf{k}|^2)$, the asymptotic behaviour of which is given by

$$g_1(|\mathbf{k}|^2) - g_2(|\mathbf{k}|^2) \sim \begin{cases} 1/45, & \text{if } k^2 \ll 1, \\ 16/3k^6, & \text{if } k^2 \gg 1. \end{cases} \quad (\text{C } 4)$$

Appendix D. Effective Hamiltonian evaluated for the order parameter hypothesis

D.1. Quadratic contribution

We now compute the contribution in the $n \rightarrow 0$ limit to the effective Hamiltonian, equation (5.12 b), that is quadratic in $\Omega_{\hat{k}}$, for the specific form of $\Omega_{\hat{k}}$ given in equation (3.14). No approximations will be made. To this end we focus on the quantity

$$\lim_{n \rightarrow 0} \frac{1}{n} \frac{2}{V^n} \sum_{\hat{k}} \dagger |\Omega_{\hat{k}}|^2. \quad (\text{D } 1)$$

Inserting $\Omega_{\hat{k}}$ from equation (3.14), we obtain

$$\begin{aligned} \frac{2}{V^n} \sum_{\hat{k}} \dagger |\Omega_{\hat{k}}|^2 &= \frac{1}{V^n} \sum_{\hat{k}} |\Omega_{\hat{k}}|^2 \\ &= \frac{1}{V^n} \sum_{\hat{k}} q^2 \int_0^\infty d\tau_1 p(\tau_1) \int_0^\infty d\tau_2 p(\tau_2) \delta_{\hat{k},0}^{(d)} \exp(-\hat{k}^2(\tau_1^{-1} + \tau_2^{-1})/2) \\ &= q^2 \int_0^\infty d\tau \int_0^\infty d\tau_1 p(\tau_1) \int_0^\infty d\tau_2 p(\tau_2) \delta(\tau - (\tau_1^{-1} + \tau_2^{-1})^{-1}) \\ &\quad \times \frac{1}{V^n} \sum_{\hat{k}} \delta_{\hat{k},0}^{(d)} \exp(-\hat{k}^2/2\tau). \end{aligned} \quad (\text{D } 2 a)$$

We now add and subtract the terms in the 0- and 1-replica sectors in order to relax the constraint on the summation over \hat{k} indicated by the overbar on the summation symbol. In fact, owing to the factor of $\delta_{\hat{k},0}^{(d)}$, the summand vanishes for \hat{k} in the 1-replica sector, so that we obtain

$$\begin{aligned} \frac{2}{V^n} \sum_{\hat{k}} \dagger |\Omega_{\hat{k}}|^2 &= -\frac{q^2}{V^n} + q^2 \int_0^\infty d\tau \int_0^\infty d\tau_1 p(\tau_1) \int_0^\infty d\tau_2 p(\tau_2) \delta(\tau - (\tau_1^{-1} + \tau_2^{-1})^{-1}) \\ &\quad \times \frac{1}{V^n} \sum_{\hat{k}} \delta_{\hat{k},0}^{(d)} \exp(-\hat{k}^2/2\tau). \end{aligned} \quad (\text{D } 2 b)$$

We now focus on the remaining, unconstrained summation on the right hand side of equation (D 2 b), which we compute via the following steps. First, we introduce an integral representation of $\delta_{\hat{k},0}^{(d)}$, namely

$$\delta_{\hat{k},0}^{(d)} = \frac{1}{V} \int_V d\mathbf{c} \exp\left(\mathbf{i}\mathbf{c} \cdot \sum_{\alpha=0}^n \mathbf{k}^\alpha\right), \quad (\text{D } 3)$$

where the integral is taken over the volume V . Then we convert the summation over \hat{k} into an integral by using

$$\frac{1}{V^{n+1}} \sum_{\hat{k}} \cdots \rightarrow \int \bar{d}\hat{k} \cdots, \quad (\text{D } 4)$$

where $\bar{d}\hat{k} \equiv \prod_{\alpha=0}^n \bar{d}\mathbf{k}^\alpha$ and $\bar{d}\mathbf{k} \equiv (2\pi)^{-d} d\mathbf{k}$, and the integral is taken over the entire \hat{k} space. Thus we obtain

$$\begin{aligned} \frac{1}{V^n} \sum_{\hat{k}} \delta_{\mathbf{k},0}^{(d)} \exp(-\hat{k}^2/2\tau) &= \int \bar{d}\hat{k} \exp(-\hat{k}^2/2\tau) \int_V d\mathbf{c} \exp\left(\mathbf{i}\mathbf{c} \cdot \sum_{\alpha=0}^n \mathbf{k}^\alpha\right) \\ &= \int_V d\mathbf{c} \left\{ \int \bar{d}\mathbf{k} \exp(-\mathbf{k} \cdot \mathbf{k}/2\tau) \exp(\mathbf{i}\mathbf{k} \cdot \mathbf{c}) \right\}^{n+1} \\ &= (\tau/2\pi)^{(n+1)d/2} \int_V d\mathbf{c} \exp\left(- (n+1)\tau\mathbf{c} \cdot \mathbf{c}/2\right) \\ &= (\tau/2\pi)^{nd/2} (1+n)^{-d/2}, \end{aligned} \quad (\text{D } 5)$$

where we have used the Gaussian integral and, in the last step, have assumed that $\tau^{-1/2} \ll V^{1/d}$ for inverse square localization lengths that are given significant weight by the distribution $p(\tau)$, equation (3.14). Thus we find

$$\begin{aligned} \frac{2}{V^n} \sum_{\hat{k}} \dagger |\Omega_{\hat{k}}|^2 &= -\frac{q^2}{V^n} + q^2 \int_0^\infty d\tau \int_0^\infty d\tau_1 p(\tau_1) \int_0^\infty d\tau_2 p(\tau_2) \delta(\tau - (\tau_1^{-1} + \tau_2^{-1})^{-1}) \\ &\quad \times (\tau/2\pi)^{nd/2} (1+n)^{-d/2}. \end{aligned} \quad (\text{D } 6)$$

As we shall need this quadratic term only in the vicinity of $n = 0$, we expand for small n using equation (4.14a), and by taking the $n \rightarrow 0$ limit we obtain

$$\lim_{n \rightarrow 0} \frac{1}{n} \frac{2}{V^n} \sum_{\hat{k}} \dagger |\Omega_{\hat{k}}|^2 = \frac{d}{2} q^2 \int_0^\infty d\tau_1 p(\tau_1) \int_0^\infty d\tau_2 p(\tau_2) \ln \left(\frac{V^{2/d}}{2\pi e} (\tau_1^{-1} + \tau_2^{-1})^{-1} \right). \quad (\text{D } 7)$$

D.2. Logarithmic contribution

We now compute the contribution in the $n \rightarrow 0$ limit to the effective Hamiltonian, equation (5.12b), that can be identified as the partition function of a single macromolecule coupled to $\Omega_{\hat{k}}$ for the specific form of $\Omega_{\hat{k}}$ given in equation (3.14). The calculation will be undertaken as a perturbation expansion in the typical inverse square localization length, to first order in this quantity. Thus, we focus on the quantity

$$\left\langle \exp \left\{ 2\mu^2 V^{-n} \sum_{\hat{k}} \dagger \text{Re} \Omega_{\hat{k}}^* \int_0^1 ds \exp(\mathbf{i}\hat{k} \cdot \hat{c}(s)) \right\} \right\rangle_{n+1}^W. \quad (\text{D } 8)$$

First, we observe that $\Omega_{\hat{k}}$ has only been introduced for $\hat{k} \cdot \hat{n} > 0$, as follows from the discussion after equation (5.5). We are therefore free to introduce $\Omega_{\hat{k}}$ for $\hat{k} \cdot \hat{n} < 0$ at our convenience, and we do so via the definition

$$\Omega_{\hat{k}} \equiv \Omega_{-\hat{k}}^* \quad \text{for } \hat{k} \cdot \hat{n} < 0. \quad (\text{D } 9)$$

This allows us to eliminate the Re operation and to extend the range of the summation in equation (D 8), which becomes

$$\left\langle \exp \left\{ \mu^2 V^{-n} \sum_{\hat{k}} \Omega_{\hat{k}} \int_0^1 ds \exp(-i\hat{k} \cdot \hat{c}(s)) \right\} \right\rangle_{n+1}^W. \quad (\text{D } 10)$$

Next, we insert $\Omega_{\hat{k}}$ from equation (3.14), which gives

$$\left\langle \exp \left\{ \mu^2 q V^{-n} \sum_{\hat{k}} \delta_{\hat{k},0}^{(d)} \int_0^\infty d\tau p(\tau) \exp(-\hat{k}^2/2\tau) \int_0^1 ds \exp(-i\hat{k} \cdot \hat{c}(s)) \right\} \right\rangle_{n+1}^W. \quad (\text{D } 11)$$

We now add and subtract the terms in the 0- and 1-replica sectors to the summation over \hat{k} in order to relax the constraint indicated by the overbar on the summation symbol. In fact, owing to the factor of $\delta_{\hat{k},0}^{(d)}$, the summand vanishes for \hat{k} in the 1-replica sector, so that we obtain

$$\exp(-\mu^2 q V^{-n}) \left\langle \exp \left\{ \mu^2 q V^{-n} \sum_{\hat{k}} \delta_{\hat{k},0}^{(d)} \int_0^\infty d\tau p(\tau) \times \exp(-\hat{k}^2/2\tau) \int_0^1 ds \exp(-i\hat{k} \cdot \hat{c}(s)) \right\} \right\rangle_{n+1}^W. \quad (\text{D } 12)$$

The next step is to make the power series expansion of the exponential in the expectation value, and make r -fold use of the integral representation of the Kronecker δ -function

$$\delta_{\mathbf{k},0}^{(d)} = \frac{1}{V} \int_V d\mathbf{c} \exp(i\mathbf{c} \cdot \mathbf{k}), \quad (\text{D } 13)$$

in which the \mathbf{c} -integral is taken over the volume V , to obtain

$$\begin{aligned} \exp(\mu^2 q V^{-n}) &\left\langle \exp \left\{ 2\mu^2 V^{-n} \sum_{\hat{k}} \dagger \text{Re} \Omega_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \right\rangle_{n+1}^W \\ &= 1 + \frac{1}{V} \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{V^{nr} r!} \sum_{\hat{k}_1, \dots, \hat{k}_r} \int_V \frac{d\mathbf{c}_1}{V} \dots \frac{d\mathbf{c}_r}{V} \exp \left(i \sum_{\rho=1}^r \mathbf{c}_\rho \cdot \sum_{\alpha=0}^n \mathbf{k}_\rho^\alpha \right) \\ &\quad \times \int_0^\infty d\tau_1 p(\tau_1) \dots d\tau_r p(\tau_r) \exp \left(-\frac{1}{2} \sum_{\rho=1}^r \frac{1}{\tau_\rho} \sum_{\alpha=0}^n |\mathbf{k}_\rho^\alpha|^2 \right) \\ &\quad \times \int_0^1 ds_1 \dots ds_r \left\langle \exp \left(-i \sum_{\rho=1}^r \sum_{\alpha=0}^n \mathbf{k}_\rho^\alpha \cdot \mathbf{c}^\alpha(s_\rho) \right) \right\rangle_{n+1}^W. \end{aligned} \quad (\text{D } 14)$$

The remaining expectation value in equation (D 14), $\langle \exp(-i \sum_{\rho=1}^r \sum_{\alpha=0}^n \mathbf{k}_\rho^\alpha \cdot \mathbf{c}^\alpha(s_\rho)) \rangle_{n+1}^W$, factorizes on the replica index, giving $\prod_{\alpha=0}^n \langle \exp(-i \sum_{\rho=1}^r \mathbf{k}_\rho^\alpha \cdot \mathbf{c}(s_\rho)) \rangle_1^W$. Each factor in this product is of the form of the expectation value computed in Appendix B, in terms of which we express the remaining expectation value in equation (D 14). The result contains an $(n+1)$ -fold product of Kronecker δ -functions, which we replace with the integral representation

$$\prod_{\alpha=0}^n \delta_{\mathbf{0}, \sum_{\rho=1}^r \mathbf{k}_\rho^\alpha} = \frac{1}{V^{n+1}} \int_V d\mathbf{m}^0 \dots d\mathbf{m}^n \exp \left(-i \sum_{\alpha=0}^n \mathbf{m}^\alpha \cdot \sum_{\rho=1}^r \mathbf{k}_\rho^\alpha \right), \quad (\text{D } 15)$$

in which each of the $(n+1)$ \mathbf{m} -integrals is taken over the volume V . Next, we convert the summations over $\{\hat{k}_1, \dots, \hat{k}_r\}$ to integrations by using equation (D 4) r times,

after which the summation on the right hand side of equation (D 14) becomes

$$\begin{aligned}
& \frac{1}{V^n} \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_r \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \frac{1}{V} \int_V \frac{d\mathbf{c}_1}{V} \cdots \frac{d\mathbf{c}_r}{V} \int_V d\mathbf{m}^0 \cdots d\mathbf{m}^n \\
& \quad \times \int \bar{d}\hat{\mathbf{k}}_1 \cdots \bar{d}\hat{\mathbf{k}}_r \exp \left(i \sum_{\alpha=0}^n \sum_{\rho=1}^r \mathbf{k}_{\rho}^{\alpha} \cdot (\mathbf{c}_{\rho} - \mathbf{m}^{\alpha}) \right) \exp \left(-\frac{1}{2} \sum_{\rho, \rho'=1}^r \mathcal{R}_{\rho\rho'}^{(r)} \sum_{\alpha=0}^n \mathbf{k}_{\rho}^{\alpha} \cdot \mathbf{k}_{\rho'}^{\alpha} \right) \\
& = \frac{1}{V^n} \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_r \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \frac{1}{V} \int_V \frac{d\mathbf{c}_1}{V} \cdots \frac{d\mathbf{c}_r}{V} \\
& \quad \times \left\{ \int_V d\mathbf{m} \int \bar{d}\mathbf{k}_1 \cdots \bar{d}\mathbf{k}_r \exp \left(i \sum_{\rho=1}^r \mathbf{k}_{\rho} \cdot (\mathbf{c}_{\rho} - \mathbf{m}) \right) \right. \\
& \quad \left. \times \exp \left(-\frac{1}{2} \sum_{\rho, \rho'=1}^r \mathcal{R}_{\rho\rho'}^{(r)} \mathbf{k}_{\rho} \cdot \mathbf{k}_{\rho'} \right) \right\}^{n+1}. \tag{D 16}
\end{aligned}$$

Here, $\mathcal{R}_{\rho\rho'}^{(r)}$ is an $(r \times r)$ -matrix-valued function of the r arclength coordinates $\{s_{\nu}\}_{\nu=1}^r$ and the r inverse square localization lengths $\{\tau_{\nu}\}_{\nu=1}^r$, defined in equation (F 1). We now focus on the quantity in this expression that is raised to the $(n+1)$ th power.

By performing the Gaussian integrations, first over $\{\mathbf{k}_1, \dots, \mathbf{k}_r\}$ and then over \mathbf{m} , we obtain

$$\begin{aligned}
& \int_V d\mathbf{m} \int \bar{d}\mathbf{k}_1 \cdots \bar{d}\mathbf{k}_r \exp \left(i \sum_{\rho=1}^r \mathbf{k}_{\rho} \cdot (\mathbf{c}_{\rho} - \mathbf{m}) \right) \exp \left(-\frac{1}{2} \sum_{\rho, \rho'=1}^r \mathcal{R}_{\rho\rho'}^{(r)} \mathbf{k}_{\rho} \cdot \mathbf{k}_{\rho'} \right) \\
& = (2\pi)^{-(r-1)d/2} (\mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)})^{-d/2} \exp \left(-\frac{1}{2} \sum_{\rho, \rho'=1}^r \mathcal{G}_{\rho\rho'}^{(r)} \mathbf{c}_{\rho} \cdot \mathbf{c}_{\rho'} \right), \tag{D 17}
\end{aligned}$$

where we have introduced the $(r \times r)$ -matrix-valued function $\mathcal{G}^{(r)}$ of the r arclength coordinates $\{s_{\nu}\}_{\nu=1}^r$ and the r inverse square localization lengths $\{\tau_{\nu}\}_{\nu=1}^r$, which is built from $\mathcal{R}^{(r)}$, equation (F 1), in a manner described in Appendix F. The Gaussian integrals in equation (D 17) are convergent, owing to the positive definiteness of the eigenvalue spectrum of $\mathcal{R}^{(r)}$ and of $\mathcal{W}^{(r)}$ for finite τ . By inserting the result (D 17) into expression (D 16) we obtain

$$\begin{aligned}
& \frac{1}{V^n} \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_r \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \frac{1}{V} \int_V \frac{d\mathbf{c}_1}{V} \cdots \frac{d\mathbf{c}_r}{V} \\
& = (2\pi)^{-(r-1)(n+1)d/2} (\mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)})^{-(n+1)d/2} \exp \left(-\frac{n+1}{2} \sum_{\rho, \rho'=1}^r \mathcal{G}_{\rho\rho'}^{(r)} \mathbf{c}_{\rho} \cdot \mathbf{c}_{\rho'} \right). \tag{D 18}
\end{aligned}$$

The quantity $\mathcal{W}^{(r)}$ is built from $\mathcal{R}^{(r)}$, equation (F 1), in a manner described in Appendix F.

Next we perform the integration over $\{\mathbf{c}_1, \dots, \mathbf{c}_r\}$. This integration is not quite Gaussian, instead being quasi-Gaussian, owing to the presence of a single *zero mode*, the eigenvalue spectrum of $\mathcal{G}^{(r)}$ containing a single zero eigenvalue, the remaining $r-1$ eigenvalues being positive definite. The presence of this zero mode can readily be ascertained by observing that from the definition of $\mathcal{G}^{(r)}$, equation (F 2 c), we identically have $\sum_{\rho'=1}^r \mathcal{G}_{\rho\rho'}^{(r)} = 0$, i.e. the normalized r -vector $(1, 1, \dots, 1)/\sqrt{r}$ is an

eigenvector of $\mathcal{C}_{\rho\rho'}^{(r)}$, with zero eigenvalue. The necessary quasi-Gaussian integral is computed in Appendix E. By using it, equation (D 18) becomes

$$\begin{aligned} & \frac{1}{V^n} \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_r \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) (2\pi)^{-(r-1)nd/2} \\ & \times (\mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)})^{-nd/2} (n+1)^{-(r-1)d/2} (r^{-1} \mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)} \widetilde{\text{Det}}^{(r)} \mathcal{C}^{(r)})^{-d/2}, \end{aligned} \quad (\text{D } 19)$$

where $\widetilde{\text{Det}}^{(r)} \mathcal{C}^{(r)}$ indicates the *quasi-determinant* of $\mathcal{C}^{(r)}$, i.e. the product of all the non-zero eigenvalues of $\mathcal{C}^{(r)}$ (see [78]). We now make use of the result, established in Appendix G, that the factor $r^{-1} \mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)} \widetilde{\text{Det}}^{(r)} \mathcal{C}^{(r)}$ is identically unity. Thus, equation (D 19) is simplified, becoming

$$\begin{aligned} & \frac{1}{V^n} \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_r \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \\ & \times (2\pi)^{-(r-1)nd/2} (\mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)})^{-nd/2} (n+1)^{-(r-1)d/2}. \end{aligned} \quad (\text{D } 20)$$

We take this expression and insert it into equation (D 14) to obtain an expression for $\langle \exp \{ 2\mu^2 V^{-n} \sum_{\hat{k}}^{\dagger} \text{Re} \Omega_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \} \rangle_{n+1}^{\text{W}}$ that is valid for $n > -1$. By expanding this result for small n , we finally obtain the desired quantity:

$$\begin{aligned} & \lim_{n \rightarrow 0} \frac{2}{nd} \ln \left\langle \exp \left\{ 2\mu^2 V^{-n} \sum_{\hat{k}}^{\dagger} \text{Re} \Omega_{\hat{k}}^* \int_0^1 ds \exp(i\hat{k} \cdot \hat{c}(s)) \right\} \right\rangle_{n+1}^{\text{W}} \\ & = (\exp(-\mu^2 q) - (1 - \mu^2 q)) \ln(V^{2/d}/2\pi e) - \exp(-\mu^2 q) \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \\ & \times \int_0^1 ds_1 \cdots ds_r \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \ln(\mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)}). \end{aligned} \quad (\text{D } 21)$$

Appendix E. Quasi-Gaussian integration

Consider the following integral,

$$\frac{1}{V} \int_V d\mathbf{c}_1 \cdots d\mathbf{c}_r \exp \left(-\frac{1}{2} \sum_{\rho, \rho'=1}^r \mathcal{C}_{\rho\rho'}^{(r)} \mathbf{c}_{\rho} \cdot \mathbf{c}_{\rho'} \right) \exp \left(-i \sum_{\rho=1}^r \mathbf{c}_{\rho} \cdot \mathbf{J}_{\rho} \right), \quad (\text{E } 1)$$

taken over r copies of the volume V , in which $\mathcal{C}^{(r)}$ has as its sole non-positive definite eigenvalue the zero eigenvalue corresponding to the r -eigenvector $(1, 1, \dots, 1)/\sqrt{r}$. We shall need both the general case, in which the sources $\{\mathbf{J}_{\rho}\}_{\rho=1}^r$ are arbitrary, and also the special case, in which the sources $\{\mathbf{J}_{\rho}\}_{\rho=1}^r$ all vanish. By working in a basis in which $\mathcal{C}^{(r)}$ is diagonal and assuming that V is sufficiently large (or, equivalently that no non-zero eigenvalue of $\mathcal{C}^{(r)}$ is arbitrarily small) one finds that this *quasi-Gaussian* integral is given by

$$r^{d/2} (2\pi)^{(r-1)d/2} (\widetilde{\text{Det}}^{(r)} \mathcal{C}^{(r)})^{-d/2} \exp \left(-\frac{1}{2} \sum_{\rho, \rho'=1}^r \tilde{\mathcal{C}}_{\rho\rho'}^{(r)} \mathbf{J}_{\rho} \cdot \mathbf{J}_{\rho'} \right) \delta_{0, \sum_{\rho=1}^d \mathbf{J}_{\rho}}, \quad (\text{E } 2)$$

where $\tilde{\mathcal{C}}^{(r)}$ is the *quasi-inverse* of $\mathcal{C}^{(r)}$, i.e. the eigenvector expansion of the inverse of $\mathcal{C}^{(r)}$ from which the term corresponding to the zero eigenvalue has been omitted (see

[78]). Similarly, as mentioned in Appendix D 2, $\widetilde{\text{Det}}^{(r)} \mathcal{G}^{(r)}$ indicates the *quasi-determinant* of $\mathcal{G}^{(r)}$ (see [78]). The factor of $r^{d/2}$ is subtle, but is familiar from the context of so-called collective coordinates. It arises from the fact that owing to the presence of the zero eigenvalue there are d integration directions for which convergence is not controlled by a Gaussian integrand. Not only do the corresponding integrations yield a volume factor, they also each yield a factor of \sqrt{r} by virtue of the limits on them determined by the form of the corresponding eigenvector. For the special case in which the sources $\{\mathbf{J}_\rho\}_{\rho=1}^r$ all vanish, we have

$$\frac{1}{V} \int_V d\mathbf{c}_1 \cdots d\mathbf{c}_r \exp \left(-\frac{1}{2} \sum_{\rho, \rho'=1}^r \mathcal{G}_{\rho\rho'}^{(r)} \mathbf{c}_\rho \cdot \mathbf{c}_{\rho'} \right) = r^{d/2} (2\pi)^{(r-1)d/2} (\widetilde{\text{Det}}^{(r)} \mathcal{G}^{(r)})^{-d/2}. \quad (\text{E } 3)$$

Appendix F. Perturbation expansion at long localization lengths: free energy

Consider the quantity $\mathcal{R}^{(r)}$, an $(r \times r)$ -matrix-valued function of the r arclength coordinates $\{s_\nu\}_{\nu=1}^r$ and the r inverse square localization lengths $\{\tau_\nu\}_{\nu=1}^r$, given by

$$\mathcal{R}_{\rho\rho'}^{(r)} \equiv \tau_\rho^{-1} \delta_{\rho\rho'} + \mathcal{S}_{\rho\rho'}, \quad (\text{F } 1)$$

where \mathcal{S} is given by equation (B 2). We have found it useful to construct from $\mathcal{R}^{(r)}$ several auxiliary quantities:

$$\mathcal{U}_\rho^{(r)} \equiv \sum_{\rho'=1}^r (\mathcal{R}^{(r)})^{-1} |_{\rho\rho'}, \quad (\text{F } 2 a)$$

$$\mathcal{W}^{(r)} \equiv \sum_{\rho=1}^r \mathcal{U}_\rho^{(r)}, \quad (\text{F } 2 b)$$

$$\mathcal{C}_{\rho\rho'}^{(r)} \equiv (\mathcal{R}^{(r)})^{-1} |_{\rho\rho'} - \mathcal{U}_\rho^{(r)} \mathcal{U}_{\rho'}^{(r)} / \mathcal{W}^{(r)}. \quad (\text{F } 2 c)$$

We shall need to develop perturbative expansions in $\{\tau_\nu\}_{\nu=1}^r$ of $\ln(\mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)})$ to linear order and of $\mathcal{C}^{(r)}$ to quadratic order. To this end, we introduce the $(r \times r)$ identity matrix $\mathcal{I}^{(r)} \equiv \delta_{\rho\rho'}$, and make the definition

$$\mathcal{R}_0^{(r)} |_{\rho\rho'} \equiv \tau_\rho^{-1} \delta_{\rho\rho'}, \quad (\text{F } 3)$$

so that $(\mathcal{R}_0^{(r)})^{-1} |_{\rho\rho'} \equiv \tau_\rho \delta_{\rho\rho'}$. First, we consider $\ln \text{Det}^{(r)} \mathcal{R}^{(r)}$:

$$\begin{aligned} \ln \text{Det}^{(r)} \mathcal{R}^{(r)} &= \ln \text{Det}^{(r)} (\mathcal{R}_0^{(r)} + \mathcal{S}) \\ &= \ln \text{Det}^{(r)} \mathcal{R}_0^{(r)} \cdot (\mathcal{I}^{(r)} + (\mathcal{R}_0^{(r)})^{-1} \cdot \mathcal{S}) \\ &= \ln \text{Det}^{(r)} \mathcal{R}_0^{(r)} + \ln \text{Det}^{(r)} (\mathcal{I}^{(r)} + (\mathcal{R}_0^{(r)})^{-1} \cdot \mathcal{S}) \\ &= \ln \text{Det}^{(r)} \mathcal{R}_0^{(r)} + \text{Tr}^{(r)} \ln (\mathcal{I}^{(r)} + (\mathcal{R}_0^{(r)})^{-1} \cdot \mathcal{S}) \\ &= \ln \left(\prod_{\rho=1}^r \tau_\rho^{-1} \right) + \text{Tr}^{(r)} ((\mathcal{R}_0^{(r)})^{-1} \cdot \mathcal{S} + \cdots) \\ &= -\sum_{\rho=1}^r \ln \tau_\rho + \sum_{\rho=1}^r \tau_\rho \mathcal{S}_{\rho\rho} + \mathcal{O}(\tau^2), \end{aligned} \quad (\text{F } 4)$$

where $\text{Tr}^{(r)}$ denotes the trace of an $r \times r$ matrix. Second, we consider $(\mathcal{R}^{(r)})^{-1}$. From equation (F 1) we have $\mathcal{R}^{(r)} = \mathcal{R}_0^{(r)} + \mathcal{S}$, from which follows the Dyson-type equation

$$(\mathcal{R}^{(r)})^{-1} = (\mathcal{R}_0^{(r)})^{-1} - (\mathcal{R}_0^{(r)})^{-1} \cdot \mathcal{S} \cdot (\mathcal{R}^{(r)})^{-1}. \quad (\text{F } 5)$$

Iterating the Dyson-type equation once and then truncating gives

$$(\mathcal{R}^{(r)})^{-1}|_{\rho\rho'} = \tau_\rho \delta_{\rho\rho'} - \tau_\rho \mathcal{S}_{\rho\rho'} \tau_{\rho'} + \mathcal{O}(\tau^3). \quad (\text{F } 6)$$

By using this result in equations (F 2 a) and (F 2 b) we obtain

$$\mathcal{U}_\rho^{(r)} = \tau_\rho - \tau_\rho \sum_{\rho'=1}^r \mathcal{S}_{\rho\rho'} \tau_{\rho'}, \quad (\text{F } 7 a)$$

$$\mathcal{W}^{(r)} = \sum_{\rho=1}^r \tau_\rho - \sum_{\rho,\rho'=1}^r \tau_\rho \mathcal{S}_{\rho\rho'} \tau_{\rho'} + \mathcal{O}(\tau^3). \quad (\text{F } 7 b)$$

Third, we use equations (F 4) and (F 7 b) to obtain

$$\ln(\mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)}) = \ln \left(\frac{\sum_{\rho=1}^r \tau_\rho}{\prod_{\rho=1}^r \tau_\rho} \right) + \left(\sum_{\rho=1}^r \tau_\rho \mathcal{S}_{\rho\rho} - \frac{\sum_{\rho,\rho'=1}^r \tau_\rho \mathcal{S}_{\rho\rho'} \tau_{\rho'}}{\sum_{\sigma=1}^r \tau_\sigma} \right) + \mathcal{O}(\tau^2). \quad (\text{F } 8)$$

Finally, by using equations (F 6), (F 7 a) and (F 7 b) in equation (F 2 c) we obtain

$$\begin{aligned} \mathcal{C}_{\rho\rho'}^{(r)} = & \left(\tau_\rho \delta_{\rho\rho'} - \frac{\tau_\rho \tau_{\rho'}}{\sum_{\sigma=1}^r \tau_\sigma} \right) \\ & + \left[-\tau_\rho \mathcal{S}_{\rho\rho'} \tau_{\rho'} + \tau_\rho \tau_{\rho'} \frac{\sum_{\nu=1}^r \tau_\nu (\mathcal{S}_{\nu\rho'} + \mathcal{S}_{\rho\nu})}{\sum_{\sigma=1}^r \tau_\sigma} - \tau_\rho \tau_{\rho'} \frac{\sum_{\nu,\nu'=1}^r \tau_\nu \tau_{\nu'} \mathcal{S}_{\nu\nu'}}{\left(\sum_{\sigma=1}^r \tau_\sigma \right)^2} \right] + \mathcal{O}(\tau^3). \quad (\text{F } 9) \end{aligned}$$

In reducing the free energy (6.9) to the form (6.13) we have used, *inter alia*, the perturbation expansion (F 8). In this way, the free energy reduces to an assembly of terms each being a functional of $p(\tau)$. Each term has a coefficient determined by integration over the arclength variables $\{s_1, \dots, s_r\}$ of integrands arising from factors of $\mathcal{S}_{\rho\rho'}$, defined in equation (B 2), which depend on the arclength variables. The necessary integrals are readily expressed in terms of the following ones:

$$\int_0^1 ds_1 \mathcal{S}_{11} = \int_0^1 ds_1 \min(s_1, s_1) = \int_0^1 ds_1 s_1 = 1/2, \quad (\text{F } 10 a)$$

$$\int_0^1 ds_1 \int_0^1 ds_2 \mathcal{S}_{12} = \int_0^1 ds_1 \int_0^1 ds_2 \min(s_1, s_2) = 2 \int_0^1 ds_1 \int_0^{s_1} ds_2 s_2 = 1/3. \quad (\text{F } 10 b)$$

Appendix G. A useful identity

We make repeated use of the identity

$$r^{-1} \mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)} \widetilde{\text{Det}}^{(r)} \mathcal{C}^{(r)} = 1, \quad (\text{G } 1)$$

where $\mathcal{R}^{(r)}$, $\mathcal{W}^{(r)}$ and $\mathcal{C}^{(r)}$ are, respectively, defined in equations (F 1), (F 2 b) and (F 2 c) of Appendix F. To derive this identity, we evaluate the following quantity (which arises, for example, in equation (D 16)) in two ways:

$$V^{-1} \int_V d\mathbf{m} \int d\mathbf{k}_1 \cdots d\mathbf{k}_r \exp\left(i \sum_{\rho=1}^r \mathbf{k}_\rho \cdot (\mathbf{c}_\rho - \mathbf{m})\right) \exp\left(-\frac{1}{2} \sum_{\rho, \rho'=1}^r \mathcal{R}_{\rho\rho'}^{(r)} \mathbf{k}_\rho \cdot \mathbf{k}_{\rho'}\right). \quad (\text{G } 2)$$

First, by integrating over $\{\mathbf{c}_\rho\}_{\rho=1}^r$, then over $\{\mathbf{k}_\rho\}_{\rho=1}^r$, and then over \mathbf{m} we obtain the result: unity. Second, by integrating over $\{\mathbf{k}_\rho\}_{\rho=1}^r$, then over \mathbf{m} , and then, by using the quasi-Gaussian integral equation (E 3), over $\{\mathbf{c}_\rho\}_{\rho=1}^r$, we obtain the result

$$(r^{-1} \mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)} \widetilde{\text{Det}}^{(r)} \mathcal{C}^{(r)})^{-d/2}, \quad (\text{G } 3)$$

and hence the identity, equation (G 1).

Appendix H. Laplace representation of free energy

In this Appendix we describe in detail how to exchange the dependence of the three contributions to \tilde{f}^{var} , equation (6.13), from $p(\tau)$ to its Laplace transform $\hat{p}(\hat{\tau})$. We begin by noting two integrals:

$$\ln \tau = \int_0^\infty \frac{d\hat{\tau}}{\hat{\tau}} (\exp(-\hat{\tau}) - \exp(-\hat{\tau}\tau)), \quad (\text{H } 1 a)$$

$$\frac{1}{\tau} = \int_0^\infty d\hat{\tau} \exp(-\hat{\tau}\tau). \quad (\text{H } 1 b)$$

The latter integral is elementary; the former is an example of a Frullanian integral (see [79]). We use equation (H 1 a) to express the first contribution to \tilde{f}^{var} as

$$\begin{aligned} \left\{ \ln \left(\frac{\tau_1 + \tau_2}{\tau_1 \tau_2} \right) \right\}_\tau &= \{\ln(\tau_1 + \tau_2) - \ln(\tau_1) - \ln(\tau_2)\}_\tau \\ &= \int_0^\infty d\tau_1 p(\tau_1) \int_0^\infty d\tau_2 p(\tau_2) \int_0^\infty \frac{d\hat{\tau}}{\hat{\tau}} (-\exp(-\hat{\tau}) - \exp(-\hat{\tau}(\tau_1 + \tau_2)) \\ &\quad + \exp(-\hat{\tau}\tau_1) + \exp(-\hat{\tau}\tau_2)) \\ &= \int_0^\infty \frac{d\hat{\tau}}{\hat{\tau}} (-\hat{p}(\hat{\tau})^2 + 2\hat{p}(\hat{\tau}) - \exp(-\hat{\tau})), \end{aligned} \quad (\text{H } 2 a)$$

where the braces $\{\dots\}_\tau$ were defined immediately following equation (6.13). By following the identical strategy, we use equation (H 1 a) to express the second contribution to \tilde{f}^{var} as

$$\begin{aligned} \left\{ \ln \left(\frac{\tau_1 + \tau_2 + \tau_3}{\tau_1 \tau_2 \tau_3} \right) \right\}_\tau &= \{\ln(\tau_1 + \tau_2 + \tau_3) - \ln(\tau_1) - \ln(\tau_2) - \ln(\tau_3)\}_\tau \\ &= \int_0^\infty \frac{d\hat{\tau}}{\hat{\tau}} (-\hat{p}(\hat{\tau})^3 + 3\hat{p}(\hat{\tau}) - 2\exp(-\hat{\tau})). \end{aligned} \quad (\text{H } 2 b)$$

To express the third contribution to \tilde{f}^{var} in terms of $\hat{p}(\hat{\tau})$ we make use of equation (H 1 b). This yields

$$\begin{aligned}
 \left\{ \frac{\tau_1 \tau_2}{\tau_1 + \tau_2} \right\}_\tau &= \int_0^\infty d\tau_1 p(\tau_1) \int_0^\infty d\tau_2 p(\tau_2) \frac{\tau_1 \tau_2}{\tau_1 + \tau_2} \\
 &= \int_0^\infty d\tau_1 p(\tau_1) \tau_1 \int_0^\infty d\tau_2 p(\tau_2) \tau_2 \int_0^\infty d\hat{\tau} \exp(-\hat{\tau}(\tau_1 + \tau_2)) \\
 &= \int_0^\infty d\hat{\tau} (d\hat{p}/d\hat{\tau})^2.
 \end{aligned} \tag{H 2 c}$$

We now take the functional derivative with respect to $\hat{p}(\hat{\tau})$ of these three contributions to \tilde{f}^{var} . Being local, the first two are straightforward to compute, respectively yielding

$$\frac{\delta}{\delta \hat{p}(\hat{\tau})} \left\{ \ln \left(\frac{\tau_1 + \tau_2}{\tau_1 \tau_2} \right) \right\}_\tau = \frac{2}{\hat{\tau}} (1 - \hat{p}(\hat{\tau})), \tag{H 3 a}$$

$$\frac{\delta}{\delta \hat{p}(\hat{\tau})} \left\{ \ln \left(\frac{\tau_1 + \tau_2 + \tau_3}{\tau_1 \tau_2 \tau_3} \right) \right\}_\tau = \frac{3}{\hat{\tau}} (1 - \hat{p}(\hat{\tau})^2). \tag{H 3 b}$$

To evaluate the functional derivative with respect to $\hat{p}(\hat{\tau})$ of the third contribution to \tilde{f}^{var} requires an integration by parts. The integrated piece vanishes because $\hat{p}(\hat{\tau})$ is to be varied at neither $\hat{\tau} = 0$ nor $\hat{\tau} = \infty$, due to the boundary conditions. Thus we obtain for the third contribution to \tilde{f}^{var} :

$$\frac{\delta}{\delta \hat{p}(\hat{\tau})} \left\{ \frac{\tau_1 \tau_2}{\tau_1 + \tau_2} \right\}_\tau = -2 \frac{d^2 \hat{p}}{d\hat{\tau}^2}. \tag{H 3 c}$$

Appendix I. Order-parameter weighted averages

In this Appendix we focus on the computation of the following quantity, defined for arbitrary \hat{l} and \hat{l}' :

$$\begin{aligned}
 &\left\langle \int_0^1 dt \exp(-i\hat{l} \cdot \hat{c}(t)) \int_0^1 dt' \exp(-i\hat{l}' \cdot \hat{c}(t')) \right. \\
 &\quad \times \exp \left\{ \mu^2 q V^{-n} \sum_{\hat{k}} \int_0^1 ds \exp(-i\hat{k} \cdot \hat{c}(s)) \delta_{\hat{k},0}^{(d)} \int_0^\infty d\tau p(\tau) \exp(-\hat{k}^2/2\tau) \right\}_{n+1}^{\text{W}}. \tag{I 1}
 \end{aligned}$$

In addition, we make two applications of it. We proceed by expanding the exponential, which yields

$$\begin{aligned}
 &\left\langle \int_0^1 dt \exp(-i\hat{l} \cdot \hat{c}(t)) \int_0^1 dt' \exp(-i\hat{l}' \cdot \hat{c}(t')) \right\rangle_{n+1}^{\text{W}} \\
 &\quad + \sum_{r=1}^\infty \frac{\mu^{2r} q^r}{V^{nr} r!} \int_0^1 ds_1 \cdots ds_{r+2} \int_0^\infty d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \\
 &\quad \times \sum_{\hat{k}_1, \dots, \hat{k}_r} \prod_{\rho=1}^r \delta_{\hat{k}_\rho, 0}^{(d)} \exp \left(-\frac{1}{2} \sum_{\rho=1}^r \frac{1}{\tau_\rho} \hat{k}_\rho^2 \right) \\
 &\quad \times \left\langle \exp(-i\hat{l} \cdot \hat{c}(s_{r+1})) \exp(-i\hat{l}' \cdot \hat{c}(s_{r+2})) \exp \left(-i \sum_{\rho=1}^r \hat{k}_\rho \cdot \hat{c}(s_\rho) \right) \right\rangle_{n+1}^{\text{W}}. \tag{I 2}
 \end{aligned}$$

Next, we observe the factorization of the Wiener measure correlators on the replica index, use the explicit result for this correlator given in Appendix B, use integral

representations for the Kronecker δ -functions [equations (D 15) and (D 13)], and convert summations to integrals by using equation (D 4), thus obtaining

$$\begin{aligned}
& \delta_{\hat{l}+\hat{l}',\hat{0}}^{(nd+d)} \int_0^1 dt \int_0^1 dt' \exp(-|t-t'| \hat{l}^2) \\
& + \frac{1}{V^n} \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_{r+2} \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \frac{1}{V} \int_V d\mathbf{c}_1 \cdots d\mathbf{c}_r \int_V d\mathbf{m}^0 \cdots d\mathbf{m}^n \\
& \times \int d\hat{\mathbf{k}}_1 \cdots d\hat{\mathbf{k}}_r \exp\left(i \sum_{\rho=1}^r \mathbf{c}_\rho \cdot \sum_{\alpha=0}^n \mathbf{k}_\rho^\alpha\right) \exp\left(-i \sum_{\alpha=0}^n \mathbf{m}^\alpha \cdot \left(\mathbf{l}^\alpha + \mathbf{l}'^\alpha + \sum_{\rho=1}^r \mathbf{k}_\rho^\alpha\right)\right) \\
& \times \exp\left(-\sum_{\rho=1}^r \hat{k}_\rho^2 / 2\tau_\rho\right) \exp\left(-\frac{1}{2} \sum_{\alpha=0}^n \sum_{\rho,\rho'=1}^r \mathbf{k}_\rho^\alpha \cdot \mathbf{k}_{\rho'}^\alpha \mathcal{S}_{\rho\rho'}\right) \exp\left(-\sum_{\alpha=0}^n \sum_{\rho=1}^r \mathbf{l}^\alpha \cdot \mathbf{k}_\rho^\alpha \mathcal{S}_{r+1,\rho}\right) \\
& \times \exp\left(-\sum_{\alpha=0}^n \sum_{\rho=1}^r \mathbf{l}'^\alpha \cdot \mathbf{k}_\rho^\alpha \mathcal{S}_{r+2,\rho}\right) \exp\left(-\frac{1}{2} \hat{l}^2 \mathcal{S}_{r+1,r+1}\right) \exp\left(-\frac{1}{2} \hat{l}'^2 \mathcal{S}_{r+2,r+2}\right) \\
& \times \exp\left(-\hat{l} \cdot \hat{l}' \mathcal{S}_{r+1,r+2}\right). \tag{I3}
\end{aligned}$$

We now recognize that the integrals over $\{\mathbf{m}^\alpha\}_{\alpha=0}^n$ and $\{\mathbf{k}_1^\alpha, \dots, \mathbf{k}_r^\alpha\}_{\alpha=0}^n$ factorize on the replica index, giving

$$\begin{aligned}
& \delta_{\hat{l}+\hat{l}',\hat{0}}^{(nd+d)} \int_0^1 dt \int_0^1 dt' \exp(-|t-t'| \hat{l}^2) + \frac{1}{V^n} \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_{r+2} \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \\
& \times \exp\left(-\frac{1}{2} \hat{l}^2 \mathcal{S}_{r+1,r+1} - \frac{1}{2} \hat{l}'^2 \mathcal{S}_{r+2,r+2} - \hat{l} \cdot \hat{l}' \mathcal{S}_{r+1,r+2}\right) \frac{1}{V} \int_V d\mathbf{c}_1 \cdots d\mathbf{c}_r \\
& \times \prod_{\alpha=0}^n \left\{ \int_V d\mathbf{m} \int d\mathbf{k}_1 \cdots d\mathbf{k}_r \exp\left(i \sum_{\rho=1}^r \mathbf{c}_\rho \cdot \mathbf{k}_\rho\right) \exp\left(-i \mathbf{m} \cdot \left(\mathbf{l}^\alpha + \mathbf{l}'^\alpha + \sum_{\rho=1}^r \mathbf{k}_\rho\right)\right) \right\} \\
& \times \exp\left(-\sum_{\rho=1}^r \mathbf{k}_\rho^2 / 2\tau_\rho\right) \exp\left(-\frac{1}{2} \sum_{\rho,\rho'=1}^r \mathbf{k}_\rho \cdot \mathbf{k}_{\rho'} \mathcal{S}_{\rho\rho'}\right) \\
& \times \exp\left(-\sum_{\rho=1}^r \mathbf{l}^\alpha \cdot \mathbf{k}_\rho \mathcal{S}_{r+1,\rho}\right) \exp\left(-\sum_{\rho=1}^r \mathbf{l}'^\alpha \cdot \mathbf{k}_\rho \mathcal{S}_{r+2,\rho}\right) \Big\}. \tag{I4}
\end{aligned}$$

At this stage we focus on the factorized integrals over $\{\mathbf{k}_\rho^\alpha\}_\rho^r$ and \mathbf{m}^α occurring under the product. As they are Gaussian integrals they can straightforwardly be performed (we prefer to integrate over $\{\mathbf{k}_\rho^\alpha\}_{\rho=1}^r$ first and \mathbf{m}^α second), yielding

$$\begin{aligned}
& (2\pi)^{-(r-1)d/2} (\mathcal{W}^{(r)}) \text{Det}^{(r)} \mathcal{Q}^{(r)-d/2} \exp\left(-|\mathbf{l}^\alpha + \mathbf{l}'^\alpha|^2 / 2\mathcal{W}^{(r)}\right) \\
& \times \exp\left(-\frac{1}{2} \sum_{\rho,\rho'=1}^r \mathcal{C}_{\rho\rho'}^{(r)}(\mathbf{c}_\rho + i\mathbf{l}^\alpha \mathcal{S}_{r+1,\rho} + i\mathbf{l}'^\alpha \mathcal{S}_{r+2,\rho}) \cdot (\mathbf{c}_{\rho'} + i\mathbf{l}^\alpha \mathcal{S}_{r+1,\rho'} + i\mathbf{l}'^\alpha \mathcal{S}_{r+2,\rho'})\right) \\
& \times \exp\left(-\frac{i}{\mathcal{W}^{(r)}} (\mathbf{l}^\alpha + \mathbf{l}'^\alpha) \cdot \sum_{\rho=1}^r \mathcal{Q}_\rho^{(r)}(\mathbf{c}_\rho + i\mathbf{l}^\alpha \mathcal{S}_{r+1,\rho} + i\mathbf{l}'^\alpha \mathcal{S}_{r+2,\rho})\right), \tag{I5}
\end{aligned}$$

where $\mathcal{Q}^{(r)}$, $\mathcal{W}^{(r)}$ and $\mathcal{C}^{(r)}$ are respectively defined in equations (F 2 a), (F 2 b) and (F 2 c). Next, we insert the result of integrating over $\{\mathbf{k}_\rho^\alpha\}_{\rho=1}^r$ and \mathbf{m}^α into equation (I4) and focus on the remaining integrals over $\{\mathbf{c}_\rho\}_{\rho=1}^r$. Just as we encountered in

Appendix D, this integration is not quite Gaussian, instead being quasi-Gaussian, owing to the presence of a single zero in the eigenvalue spectrum of $\mathcal{C}^{(r)}$. The necessary quasi-Gaussian integral is computed in Appendix E. By using it, equation (I 4) becomes

$$\begin{aligned}
 & \delta_{\hat{l}+\hat{l}',\hat{0}}^{(nd+d)} \int_0^1 dt \int_0^1 dt' \exp(-|t-t'|^2) \\
 & + \delta_{\hat{l}+\hat{l}',\mathbf{0}}^{(d)} \frac{1}{V^n} \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_{r+2} \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \\
 & \times (2\pi)^{-(r-1)nd/2} (\mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)})^{-nd/2} (n+1)^{-(r-1)d/2} \\
 & \times (r^{-1} \mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)} \widetilde{\text{Det}}^{(r)} \mathcal{C}^{(r)})^{-d/2} \\
 & \times \exp \left\{ (\mathcal{W}^{(r)})^{-1} \sum_{\rho=1}^r \mathcal{Q}_{\rho}^{(r)} (\hat{l}^2 \mathcal{S}_{r+1,\rho} + \hat{l}'^2 \mathcal{S}_{r+2,\rho} + \hat{l} \cdot \hat{l}' (\mathcal{S}_{r+1,\rho} + \mathcal{S}_{r+2,\rho})) \right\} \\
 & \times \exp(-(\hat{l}^2 \mathcal{S}_{r+1,r+1} + \hat{l}'^2 \mathcal{S}_{r+2,r+2} + 2\hat{l} \cdot \hat{l}' \mathcal{S}_{r+1,r+2})/2) \\
 & \times \exp \left(\frac{1}{2} \hat{l}^2 \sum_{\rho,\rho'=1}^r \mathcal{C}_{\rho\rho'}^{(r)} \mathcal{S}_{r+1,\rho} \mathcal{S}_{r+1,\rho'} + \frac{1}{2} \hat{l}'^2 \sum_{\rho,\rho'=1}^r \mathcal{C}_{\rho\rho'}^{(r)} \mathcal{S}_{r+2,\rho} \mathcal{S}_{r+2,\rho'} \right. \\
 & \left. + \hat{l} \cdot \hat{l}' \sum_{\rho,\rho'=1}^r \mathcal{C}_{\rho\rho'}^{(r)} \mathcal{S}_{r+1,\rho} \mathcal{S}_{r+2,\rho'} \right) \exp(-(\hat{l}^2 + \hat{l}'^2 + 2\hat{l} \cdot \hat{l}')/2 \mathcal{W}^{(r)}) \\
 & \times \exp \left(-(n+1)^{-1} \sum_{\rho,\rho'=1}^r \mathcal{C}_{\rho\rho'}^{(r)} (\bar{\mathbf{I}} \mathcal{S}_{r+1,\rho} + \bar{\mathbf{V}} \mathcal{S}_{r+2,\rho}) \cdot (\bar{\mathbf{I}} \mathcal{S}_{r+1,\rho'} + \bar{\mathbf{V}} \mathcal{S}_{r+2,\rho'})/2 \right). \quad (\text{I } 6)
 \end{aligned}$$

We have simplified this result by making use of the identity given in equation (G 1) of Appendix G. We have further simplified it by observing that as $\tilde{\mathcal{C}}^{(r)}$ is the quasi-inverse [78] of $\mathcal{C}^{(r)}$ (see Appendix F and [78]), the relevant zero-mode being $(1, 1, \dots, 1)/\sqrt{r}$, we have

$$\tilde{\mathcal{C}}^{(r)} \cdot \mathcal{C}^{(r)}|_{\rho\rho'} = \delta_{\rho\rho'} - r^{-1}, \quad (\text{I } 7 a)$$

$$\mathcal{C}^{(r)} \cdot \tilde{\mathcal{C}}^{(r)} \cdot \mathcal{C}^{(r)} = \mathcal{C}^{(r)}. \quad (\text{I } 7 b)$$

In addition, we have used the fact that there is a single zero mode to ascertain that $\widetilde{\text{Det}}^{(r)}((n+1)\mathcal{C}^{(r)}) = (n+1)^{r-1} \widetilde{\text{Det}}^{(r)} \mathcal{C}^{(r)}$.

As our first application of equation (I 6), we set $\hat{l} = \hat{l}' = \hat{0}$, thus obtaining a normalization factor that we shall use subsequently:

$$\begin{aligned}
 & 1 + \frac{1}{V^n} \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_{r+2} \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \\
 & \times (2\pi)^{-(r-1)nd/2} (\mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)})^{-nd/2} (n+1)^{-(r-1)d/2}. \quad (\text{I } 8)
 \end{aligned}$$

As our second application of equation (I 6) we compute the right hand side of equation (6.25) by forming the quotient of equation (I 6) with $\hat{l}' = \hat{0}$ and equation (I 8). By making use of the identity equation (G 1) and taking the limit $n \rightarrow 0$ we obtain equations (6.26 a) and (6.26 b).

Appendix J. Perturbation expansion at long localization lengths: order parameter

In this Appendix we compute the perturbative expansions of $\Upsilon^{(1)}$ and $\Upsilon^{(2)}$ needed to compute the right hand side of equation (6.28). By using the definitions (B 2), (F 2 a), (F 2 b) and (F 2 c), we find

$$\Upsilon^{(1)} = (\tau_1^{-1} + |s_1 - s_2|)^{-1} = \tau_1 - |s_1 - s_2| \tau_1^2 + \mathcal{O}(\tau^3), \quad (\text{J } 1 \text{ a})$$

$$\Upsilon^{(2)} = \tau_1 + \tau_2 + \mathcal{O}(\tau^2). \quad (\text{J } 1 \text{ b})$$

By inserting these results into equation (6.28), and using equation (6.27), we obtain

$$\begin{aligned} \underline{q}p(\tau) = & (1 - q)\mu^2 q \int_0^1 ds_1 ds_2 \int_0^\infty d\tau_1 p(\tau_1) \delta(\tau - \tau_1 + \tau_1^2 |s_1 - s_2|) \\ & + \frac{1}{2} \mu^4 q^2 \int_0^1 ds_1 ds_2 ds_3 \int_0^\infty d\tau_1 p(\tau_1) d\tau_2 p(\tau_2) \delta(\tau - \tau_1 - \tau_2) + \mathcal{O}(\epsilon^2). \end{aligned} \quad (\text{J } 2)$$

Next, we expand the Dirac δ -function, $\delta(\tau - \tau_1 + \tau_1^2 |s_1 - s_2|) \approx \delta(\tau - \tau_1) + \tau_1^2 |s_1 - s_2| \delta'(\tau - \tau_1)$, and perform the τ and s integrals. (Equivalently, we take the Laplace transform of equation (J 2), expand the resulting exponential function, perform the τ and s integrals, and back-transform the resulting nonlinear ordinary differential equation.) Finally, we transform to the scaling form $\pi(\theta)$ defined in equation (6.20 a), and observe that it satisfies equation (6.24 a).

Appendix K. Correlator for one-replica sector fluctuations

In this Appendix we compute the quantity \mathcal{G}_q defined in equation (7.1 b) for $\Omega_{\hat{k}}$ taking the form given in equation (3.14). Ultimately, we shall be concerned with the behaviour at small n of the diagonal and off-diagonal elements of \mathcal{G}_q via the quantities $H_{\hat{k}}^{(1)}$ and $h_{\hat{k}}^{(1)}$ defined in equations (7.11 a) and (7.11 b).

First, we note that by using the invariance under $\hat{k} \rightarrow -\hat{k}$ of the hypothesis for $\Omega_{\hat{k}}$, equation (3.14), along with the adding and subtracting of terms in the 0-replica sector, so as to relax the constraints on the summations $\sum_{\hat{k}}^\dagger$ in the exponents in the numerator and denominator of equation (7.1 b), we arrive at the form

$$\begin{aligned} & \left\langle \int_0^1 dt \exp(i\mathbf{q} \cdot \mathbf{c}^\alpha(t)) \int_0^1 dt' \exp(-i\mathbf{q} \cdot \mathbf{c}^{\alpha'}(t')) \right. \\ & \times \exp \left\{ \mu^2 q V^{-n} \sum_{\hat{k}} \int_0^1 ds \exp(-i\hat{k} \cdot \hat{c}(s)) \delta_{\hat{k}, \mathbf{0}}^{(d)} \int_0^\infty d\tau p(\tau) \exp(-\hat{k}^2/2\tau) \right\} \Bigg\rangle_{n+1}^W \\ \mathcal{G}_q^{\alpha\alpha'} = & \frac{\left\langle \int_0^1 dt \exp(i\mathbf{q} \cdot \mathbf{c}^\alpha(t)) \int_0^1 dt' \exp(-i\mathbf{q} \cdot \mathbf{c}^{\alpha'}(t')) \right.}{\left\langle \exp \left\{ \mu^2 q V^{-n} \sum_{\hat{k}} \int_0^1 ds \exp(-i\hat{k} \cdot \hat{c}(s)) \delta_{\hat{k}, \mathbf{0}}^{(d)} \int_0^\infty d\tau p(\tau) \exp(-\hat{k}^2/2\tau) \right\} \right\rangle_{n+1}^W}. \end{aligned} \quad (\text{K } 1)$$

Second, we set $\hat{l} = \{-\mathbf{q}, \mathbf{0}, \dots, \mathbf{0}\}$ and $\hat{l}' = \{\mathbf{q}, \mathbf{0}, \dots, \mathbf{0}\}$ to obtain the replica-diagonal elements of the numerator correlator in equation (K 1):

$$\begin{aligned}
 g_0(|\mathbf{q}|^2) + \frac{1}{V^n} \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_{r+2} \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \\
 \times (2\pi)^{-(r-1)nd/2} (\mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)})^{-nd/2} (n+1)^{-(r-1)d/2} \\
 \times \exp \left\{ -\frac{1}{2} q^2 \left((\mathcal{S}_{r+1,r+1} + \mathcal{S}_{r+2,r+2} - 2\mathcal{S}_{r+1,r+2}) \right. \right. \\
 \left. \left. - \frac{n}{n+1} \sum_{\rho,\rho'=1}^r \mathcal{C}_{\rho\rho'}^{(r)} (-\mathcal{S}_{r+1,\rho} + \mathcal{S}_{r+2,\rho}) (-\mathcal{S}_{r+1,\rho'} + \mathcal{S}_{r+2,\rho'}) \right) \right\}. \quad (\text{K } 2)
 \end{aligned}$$

Third, we set $\hat{l} = \{-\mathbf{q}, \mathbf{0}, \mathbf{0}, \dots, \mathbf{0}\}$ and $\hat{l}' = \{\mathbf{0}, \mathbf{q}, \mathbf{0}, \dots, \mathbf{0}\}$ to obtain the replica-off-diagonal elements of the numerator correlator in equation (K 1):

$$\begin{aligned}
 \delta_{\mathbf{q},\mathbf{0}}^{(d)} + \frac{1}{V^n} \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_{r+2} \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \\
 \times (2\pi)^{-(r-1)nd/2} (\mathcal{W}^{(r)} \text{Det}^{(r)} \mathcal{R}^{(r)})^{-nd/2} (n+1)^{-(r-1)d/2} \\
 \times \exp \left\{ -\frac{1}{2} q^2 \left((\mathcal{S}_{r+1,r+1} + \mathcal{S}_{r+2,r+2}) + \frac{2}{\mathcal{W}^{(r)}} - \frac{2}{\mathcal{W}^{(r)}} \sum_{\rho=1}^r \mathcal{W}_{\rho}^{(r)} (\mathcal{S}_{r+1,\rho} + \mathcal{S}_{r+2,\rho}) \right. \right. \\
 \left. \left. - \frac{n}{n+1} \sum_{\rho,\rho'=1}^r \mathcal{C}_{\rho\rho'}^{(r)} (\mathcal{S}_{r+1,\rho} \mathcal{S}_{r+1,\rho'} + \mathcal{S}_{r+2,\rho} \mathcal{S}_{r+2,\rho'}) - \frac{2}{n+1} \sum_{\rho,\rho'=1}^r \mathcal{C}_{\rho\rho'}^{(r)} \mathcal{S}_{r+1,\rho} \mathcal{S}_{r+2,\rho'} \right) \right\}. \quad (\text{K } 3)
 \end{aligned}$$

Next, by using the denominator, equation (I 8), and respective numerators, equations (K 2) and (K 3), we build the diagonal and off-diagonal elements, $H_{\mathbf{k}}^{(1)}$ and $h_{\mathbf{k}}^{(0)}$, of $\mathcal{G}_{\mathbf{q}}$, equation (K). At this stage, all dependence on n is explicit. Thus, by making series expansions in n about $n=0$ of the denominator and respective numerators we are able to identify $H_{\mathbf{k}}^{(0)}$, $H_{\mathbf{k}}^{(1)}$ and $h_{\mathbf{k}}^{(0)}$ of equations (7.11 a) and (7.11 b) (for $\mathbf{q} \neq \mathbf{0}$):

$$H_{\mathbf{q}}^{(0)} = g_0(|\mathbf{q}|^2), \quad (\text{K } 4 \text{ a})$$

$$\begin{aligned}
 H_{\mathbf{q}}^{(1)} = \exp(-\mu^2 q) \sum_{r=2}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_{r+2} \exp(-q^2 |s_{r+1} - s_{r+2}|/2) \\
 \times \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \\
 \times (q^2/2) \sum_{\rho,\rho'=1}^r \mathcal{C}_{\rho\rho'}^{(r)} (-\mathcal{S}_{r+1,\rho} + \mathcal{S}_{r+2,\rho}) (-\mathcal{S}_{r+1,\rho'} + \mathcal{S}_{r+2,\rho'}), \quad (\text{K } 4 \text{ b})
 \end{aligned}$$

$$\begin{aligned}
 h_{\mathbf{q}}^{(0)} = \exp(-\mu^2 q) \sum_{r=1}^{\infty} \frac{\mu^{2r} q^r}{r!} \int_0^1 ds_1 \cdots ds_{r+2} \int_0^{\infty} d\tau_1 p(\tau_1) \cdots d\tau_r p(\tau_r) \\
 \times \exp \left\{ -q^2 \left(\frac{1}{2} (\mathcal{S}_{r+1,r+1} + \mathcal{S}_{r+2,r+2}) + \frac{1}{\mathcal{W}^{(r)}} - \frac{1}{\mathcal{W}^{(r)}} \sum_{\rho=1}^r \mathcal{W}_{\rho}^{(r)} (\mathcal{S}_{r+1,\rho} + \mathcal{S}_{r+2,\rho}) \right. \right. \\
 \left. \left. - \sum_{\rho,\rho'=1}^r \mathcal{C}_{\rho\rho'}^{(r)} \mathcal{S}_{r+1,\rho} \mathcal{S}_{r+2,\rho'} \right) \right\}. \quad (\text{K } 4 \text{ c})
 \end{aligned}$$

Here we have restricted our attention to $\mathbf{q} \neq \mathbf{0}$, which is all that is necessary, and have used the fact that $\mathcal{G}^{(1)}$ vanishes identically.

As a final component of this Appendix, we expand $H_{\mathbf{q}}^{(1)}$ and $h_{\mathbf{q}}^{(0)}$, assuming that the gel fraction q and the inverse square localization lengths to which $p(\tau)$ gives appreciable weight are both asymptotically of order ϵ ($\ll 1$), which is appropriate in the vicinity of the transition, as we can verify *a posteriori*. The accuracy to which $H_{\mathbf{q}}^{(1)}$ and $h_{\mathbf{q}}^{(0)}$ must be computed can be established by observing the manner in which they appear in equation (7.15), from which we see that $\tilde{f}^{\text{gd}}\{q, p\}$ can be computed to $\mathcal{O}(\epsilon^3)$ by computing $H_{\mathbf{q}}^{(1)}$ to $\mathcal{O}(\epsilon^3)$ and $h_{\mathbf{q}}^{(0)}$ to $\mathcal{O}(\epsilon^2)$.

We first focus on $H_{\mathbf{q}}^{(1)}$. As we see from equation (F 9), $\mathcal{G}_{\rho\rho'}^{(r)}$ is of order τ , so that we need retain only the $r = 2$ term in equation (K 4 b). Thus, to sufficient accuracy we obtain

$$\begin{aligned} H_{\mathbf{q}}^{(1)} &= \frac{1}{4} q^2 \mu^4 q^2 \int_0^1 ds_3 ds_4 \exp(-q^2 |s_3 - s_4|/2) \\ &\quad \times \int_0^1 ds_1 ds_2 \sum_{\rho, \rho'=1}^2 (-\mathcal{S}_{3,\rho} + \mathcal{S}_{4,\rho})(-\mathcal{S}_{3,\rho'} + \mathcal{S}_{4,\rho'}) \left\{ \tau_{\rho} \delta_{\rho\rho'} - \frac{\tau_{\rho} \tau_{\rho'}}{\tau} \right\}_{\tau} \\ &= \frac{1}{2} \mu^4 Q^2 \left\{ \frac{\tau_1 \tau_2}{\tau_1 + \tau_2} \right\}_{\tau} q^2 (g_1(|\mathbf{q}|^2) - g_2(|\mathbf{q}|^2)), \end{aligned} \quad (\text{K } 5)$$

where the braces $\{\dots\}_{\tau}$ were defined immediately following equation (6.13) and the functions $g_1(|\mathbf{q}|^2)$ and $g_2(|\mathbf{q}|^2)$ are given by elementary integrals defined in Appendix C. Note the convenient factorization into \mathbf{q} -dependent and $p(\tau)$ -dependent terms.

Last, we focus on $h_{\mathbf{q}}^{(0)}$, for which we also need only retain terms with $r \leq 2$. However, the $r = 1$ term is not identically zero and, as it carries only a single power of q , care must be taken to compute it with appropriate accuracy. (In practice, the absence of matrix algebra renders the perturbative calculation of $(\mathcal{A}^{(1)})^{-1}$ and quantities built from it straightforward.) Thus, to sufficient accuracy, we obtain

$$\begin{aligned} h_{\mathbf{q}}^{(0)} &= (1 - \mu^2 q) \mu^2 q \{ \exp(-q^2/\tau_1) \}_{\tau} \int_0^1 ds_1 ds_2 ds_3 \exp(-q^2(|s_2 - s_1| + |s_3 - s_1|)/2) \\ &\quad + \frac{1}{2} \mu^4 q^2 \left\{ \exp(-q^2/(\tau_1 + \tau_2)) \right\}_{\tau} \int_0^1 ds_1 ds_2 ds_3 ds_4 \exp(-q^2(s_3 + s_4)/2) \\ &\quad \times \exp\left(-q^2(\tau_1 + \tau_2)^{-2} \sum_{\rho, \rho'=1}^2 \tau_{\rho} \tau_{\rho'} \mathcal{S}_{\rho\rho'}\right) \exp\left(q^2(\tau_1 + \tau_2)^{-1} \sum_{\rho=1}^2 \tau_{\rho} (\mathcal{S}_{3,\rho} + \mathcal{S}_{4,\rho})\right) \Big\}_{\tau}. \end{aligned} \quad (\text{K } 6)$$

References and notes

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- [21] As, in the context of non-interacting macromolecules, the statistical weight of a semi-microscopic configuration $\{\mathbf{c}_i(s)\}_{i=1}^N$ is simply proportional to the number of microscopic configurations consistent with it, $-k_B H_1^W$ is an entropy, and therefore does not carry a factor of $1/T$.
- [22] It is straightforward to see that in terms of dimensionful variables the Edwards measure takes the form
- $$\exp \left\{ -\frac{d}{2} \sum_{i=1}^N \int_0^L \frac{d\sigma}{\ell} \left| \frac{d}{d\sigma} \mathbf{R}_i(\sigma) \right|^2 - \frac{u_0}{2} \sum_{i,i'=1}^N \int_0^L \frac{d\sigma}{\ell} \int_0^L \frac{d\sigma'}{\ell} \delta^{(d)}(\mathbf{R}_i(\sigma) - \mathbf{R}_{i'}(\sigma')) \right\},$$
- where the excluded-volume parameter u_0 is given by $u_0 = (\ell L/d)^{d/2} (\ell/L)^2 \lambda^2$, the units of which are those of volume.
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- [24] At the microscopic level, a pair of monomers participating in a crosslink are not located at precisely the same position, being instead separated by the length of the bond that connects them. At the semi-microscopic level, however, positions are not resolved beyond a scale of order ℓ . Thus, it is adequate to model the constraints via the Dirac δ -function. A more detailed description, involving the modelling of the constraint via a function that varies on the scale of the bond-length, would yield a theory that differs only at scales of the order of ℓ : the results of the present semi-microscopic approach would thus be unchanged.
- [25] Two remarks are in order here. As a point of practice, only crosslink locations that differ by more than ℓ can be distinguished in our semi-microscopic approach. Besides, as a point of principle, the set of possible crosslink locations is discrete, owing to the underlying quantum-mechanical nature of the chemical bonds. Thus, the cluster index a is discrete. If it were continuous, one would reasonably expect that for all cluster species (other than the uncrosslinked species) the likelihood of having more than one specimen would be zero.

- [26] The thermodynamic limit ($N \rightarrow \infty$, $V \rightarrow \infty$, N/V fixed, μ^2 fixed) will eventually be taken, in a manner that is discussed in detail in section 6.2.
- [27] This can be achieved, for example, by some suitable photochemical process. Such schemes have the virtue that they are accurately determined by the equilibrium properties of the system prior to crosslinking. To describe crosslinking processes that are not simultaneous and instantaneous would require information pertaining to the kinetics of the system as the number of crosslinks grows.
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- [39] This hypothesis amounts to adopting the form $\Omega_{\vec{k}} = (1 - q) \delta_{\vec{k}, \vec{0}} + q \delta_{\vec{k}, \vec{0}}(\vec{k}^2)$, subject to the mild technical restriction that (z) be analytic for $\text{Re } z \geq 0$ and vanish sufficiently fast at infinity so as to guarantee that (z) can be expressed as the Laplace transform of another function (see, for example, [40]).
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- $$(1 - q) \delta_{\vec{k}, \vec{0}}^{(nd+d)} + q \delta_{\vec{k}, \vec{0}}^{(d)} \int_0^\infty da_0 da_1 P(a_0, a_1) \exp \left((a_0 + a_1) \sum_{\alpha \cap \beta = 0} \mathbf{k}^\alpha \cdot \mathbf{k}^\beta + a_1 \sum_{\alpha \cap \beta = 1} \mathbf{k}^\alpha \cdot \mathbf{k}^\beta \right),$$
- where $\sum_{\alpha \cap \beta = r}$ means a sum over pairs of replicas in blocks of type r ($r = 1$ indicating the nearer-diagonal type) and size $(1 + mn)$ (with $0 < m < 1$), as well as its many-step replica-symmetry-breaking generalizations.
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- [50] See, for example, J. Zinn-Justin, 1989, *Quantum Field Theory and Critical Phenomena* (Oxford: Clarendon Press), especially chap. 5.
- [51] It may seem strange that $\{\mathbf{k}^0, \mathbf{k}^1, \dots, \mathbf{k}^g\}$ can be kept fixed in equation (4.19) as $n \rightarrow 0$. However, in practice the computation of this limit generally involves quantities of the form $w(n, \sum_{a=0}^g \mathbf{k}^a, \sum_{a=0}^g |\mathbf{k}^a|^2) = w(n, \bar{\mathbf{l}}, \bar{l}^2)$, and one can simply take the limit for the first variable, while keeping the other two constant.
- [52] A different field-theoretic treatment, intended for the well-crosslinked regime (in which the many-macromolecule system is modelled by a single, linear, self-crosslinked macromolecule) can be found in [14]. For a review of this work, see [15].
- [53] At first sight it would appear convenient to scale the dummy (field) variables $\Omega_{\mathbf{k}}^\alpha, \Omega_{\hat{k}}$ and $\omega_{\mathbf{k}}$ so that no parameters arise in the exponents in equations (5.10 a), (5.10 b) and (5.10 c). However, as we shall see in equations (5.16 a) and (5.16 b), the present choice of scale leads to there being a simple connection between the fields and the physical order parameter.
- [54] A related form for the effective Hamiltonian was constructed in [8, 9].
- [55] We believe that this is the appropriate order in which to take the thermodynamic and replica limits, although this order is opposite to that commonly used in the context of spin glass theory (see, for example, section 3C of the second citation in [33]).
- [56] We have not explored the curious feature of the non-positive definiteness of \hat{k}^2 , which arises for modes, say, in the $(n-2)$ -replica sector. In principle, this feature could modify the notion that the least stable modes are the long wavelength modes.
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- [61] It is noteworthy that a divergent length scale emerges already at the level of mean-field theory. The analysis of fluctuations around the saddle-point solution would presumably reveal a second length scale, the conventional correlation length, which characterizes the decay of order-parameter correlations. It is not clear at present whether these two length scales are related.
- [62] See, for example, T. W. Körner, 1988, *Fourier Analysis* (Cambridge: Cambridge University Press), section 75.
- [63] Equation (6.23) was integrated numerically using the Bulirsch-Stoer method [65]. Choosing the solution that satisfies the boundary conditions is a delicate matter because the differential equation is unstable in the following sense. Assuming that $\hat{\pi}(0) = 1$, there is a unique value of $d\hat{\pi}/d\hat{\theta}|_{\hat{\theta}=0}$ that gives rise to $\hat{\pi}(\infty) = 0$: if $d\hat{\pi}/d\hat{\theta}|_{\hat{\theta}=0}$ is larger then $\hat{\pi}(\hat{\theta})$ will oscillate indefinitely about unity; if $d\hat{\pi}/d\hat{\theta}|_{\hat{\theta}=0}$ is smaller then $\hat{\pi}(\hat{\theta})$ will become negative and diverge to $-\infty$. We determined $d\hat{\pi}/d\hat{\theta}|_{\hat{\theta}=0}$ by using a variant of the shooting method for which we defined a monotonic function $t(x)$ via (i) $t(x) = 1/\theta^*$ if integrating equation (6.23) with $\hat{\pi}(0) = 1$ and $d\hat{\pi}/d\hat{\theta}|_{\hat{\theta}=0} = x$ gives a solution for which $\hat{\pi}(\hat{\theta}^*) = 1$ and $0 < \hat{\pi}(\hat{\theta}) < 1$ for $0 < \hat{\theta} < \hat{\theta}^*$, and (ii) $t(x) = -1/\theta^*$ if integrating equation (6.23) with $\hat{\pi}(0) = 1$ and $d\hat{\pi}/d\hat{\theta}|_{\hat{\theta}=0} = x$ gives a solution for which $\hat{\pi}(\hat{\theta}^*) = 0$ and $0 < \hat{\pi}(\hat{\theta}) < 1$ for $0 < \hat{\theta} < \hat{\theta}^*$. We identified the desired value of $d\hat{\pi}/d\hat{\theta}|_{\hat{\theta}=0}$ as the root of $t(x) = 0$.

- [64] Equation (6.24 a) was also integrated numerically using the Bulirsch–Stoer method [65]. To satisfy the normalization condition we first analytically obtained the asymptotic solution of equation (6.23) for $\hat{\theta} \gg 1$. We identified the numerical prefactor by comparison with the numerical solution, and then inverse-Laplace-transformed this asymptotic form to obtain $\pi(\theta) \sim 4.554\theta^{-2} \exp(-2/\theta)$ (for $\theta \ll 1$). We used this form to start the integration of equation (6.24 a) at a small but non-zero value of θ , thus avoiding the singularity at $\theta = 0$. After integrating to obtain the full function $\pi(\theta)$ we computed $\int_0^\infty d\theta \pi(\theta)$ numerically, and verified (to within numerical accuracy) that the value was unity. As a second check, we computed $\hat{\pi}(\theta)$ as the (numerical) Laplace transform of our (numerically obtained) solution of equation (6.24 a), and established that it coincided (to within numerical accuracy) with the numerical solution of equation (6.23).
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- [78] Let \mathcal{M} be a real and symmetric but otherwise arbitrary $r \times r$ matrix, having elements $\mathcal{M}_{\rho,\rho'}$. Let $\{m^j\}_{j=1}^r$ be a complete set of orthonormal eigenvectors, having components $\{m^j_\rho\}_{\rho=1}^r$, and let $\{\mu^j\}_{j=1}^r$ be the set of corresponding eigenvalues. The quasi-determinant $\widetilde{\text{Det}}^{(r)} \mathcal{M}$ and quasi-inverse $\tilde{\mathcal{M}}$ associated with \mathcal{M} are extensions of the standard determinant and inverse of \mathcal{M} that are relevant if \mathcal{M} is singular (i.e., has one or more vanishing eigenvalues, which we refer to as zero modes). They can be expressed as

$$\widetilde{\text{Det}}^{(r)} \mathcal{M} \equiv \prod_{j=1, (\mu^j \neq 0)}^r \mu^j, \quad \tilde{\mathcal{M}}_{\rho,\rho'} \equiv \sum_{j=1, (\mu^j \neq 0)}^r \frac{m^j_\rho m^j_{\rho'}}{\mu^j},$$

terms corresponding to vanishing eigenvalues being omitted from the product and summation. Thus, in contrast with their conventional counterparts, the quasi-determinant fails to vanish and the quasi-inverse continues to exist for singular matrices.

- [79] See, for example, Daniel Zwillinger, 1992, *Handbook of Integration* (London: Jones and Bartlett), section 35.