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Density-correlator signatures of the vulcanization transition

W. Peng and P.M. Goldbart[a]

Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080, USA

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Abstract. Certain density correlators, measurable *via* various experimental techniques, are studied in the context of the vulcanization transition. It is shown that these correlators contain essential information about both the vulcanization transition and the emergent amorphous solid state. Contact is made with various physical ingredients that have featured in experimental studies of amorphous colloidal and gel systems and in theoretical studies of the glassy state.

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1 Introduction and basic ingredients

The vulcanization transition (VT) is an equilibrium phase transition from a liquid state of matter to an amorphous solid state. It occurs when a sufficient number of permanent random constraints (*e.g.* chemical crosslinks) – the quenched randomness – are introduced to connect the constituents (*e.g.* macromolecules) whose locations are the thermally fluctuating variables. A rather detailed description of the VT has emerged over the past few years, ranging from a mean-field theory of the emerging amorphous solid state [1–5] to the critical properties of the VT itself [6].

The purpose of the present paper is to investigate the properties of correlators that solely involve the local monomer density, and to examine the extent to which such correlators provide access to informative signatures of the VT and the emergent amorphous solid state. Along the way, we shall explore the relationship of these density correlators to various experimental probes, and also discuss their relationship to the diagnostics of "non-ergodic media" studied by Pusey, Van Megen and collaborators in their work on amorphous states of colloidal and gel systems [7]. We note that density correlators closely related to the ones we shall be considering also feature in certain recent approaches to structural glasses [8], and we shall touch upon the relationship between our results and those of these recent approaches.

Apart from their connections with related studies by other researchers, we are motivated to explore the properties of density correlators in the context of the VT for the following reason. From the theoretical perspective, the natural collective coordinate from which to view the VT is *not* the local density; rather it is the amorphous solid order parameter, which becomes nonzero as the amorphous solid state is entered and whose correlator-decay properties directly mark the onset of amorphous solidification. However, as we shall discuss further below, from the perspective of experiment, the amorphous solid order parameter is rather more elusive than one would like, the most direct way to measure it being *via* incoherent quasi-elastic neutron scattering, whereas probes that couple to the density are more plentiful. For this reason, we wish to examine density correlators in the vicinity of the VT, and the extent to which they can provide access to both the structure of the amorphous solid state and the long-ranged amorphous solid order-parameter correlations that develop near the VT.

The approach that we shall adopt to study these density correlators is based upon a minimal model that takes into account the integrity of the macromolecules, their thermal position-fluctuations, the short-range repulsion of the constituent monomers, and the permanent random constraints imposed by crosslinking. This minimal model has previously been shown to give an accurate picture of the universal properties of the VT, in the sense that its predictions for the mean-field properties of the amorphous solid state have been verified in the computer simulations of Barsky and Plischke [9,10], and those of its critical properties that have been elucidated so far (*i.e.* the percolative aspects) are in accordance with the predictions of percolation and related field-theoretic approaches [11]. In order for our discussion to be concrete and physical, we shall adopt language specific to randomly crosslinked macromolecular systems (RCMSs), although our results apply to a broader class of systems.

[a] e-mail: goldbart@uiuc.edu

Let us now turn to the issue of the order parameter for the VT. This order parameter is crafted to detect and diagnose amorphous solidification; it is the following function of A wavevectors $\{\mathbf{k}^1, \mathbf{k}^2, \cdots, \mathbf{k}^A\}$:

$$\left[\frac{1}{N}\sum_{j=1}^{N}\int_0^1 \mathrm{d}s \left\langle \exp \mathrm{i}\mathbf{k}^1 \cdot \mathbf{c}_j(s)\right\rangle_\chi \left\langle \exp \mathrm{i}\mathbf{k}^2 \cdot \mathbf{c}_j(s)\right\rangle_\chi \cdots \left\langle \exp \mathrm{i}\mathbf{k}^A \cdot \mathbf{c}_j(s)\right\rangle_\chi\right], \quad (1.1)$$

where N is the total number of macromolecules, $\mathbf{c}_j(s)$ (with $j = 1, \ldots, N$ and $0 \leq s \leq 1$) is the position in d-dimensional space of the monomer at fractional arclength s along the jth macromolecule, $\langle \cdots \rangle_\chi$ denotes a thermal average for a particular realization χ of the quenched disorder (*i.e.* the crosslinking), and $[\cdots]$ represents a suitable averaging over realizations of the quenched disorder. As discussed in detail in reference [4], this order parameter does indeed detect and diagnose the amorphous solid state.

Why is the amorphous solid order parameter measurable in neutron scattering experiments? In quasi-elastic neutron scattering the *incoherent* contribution of the scattering cross-section is proportional to

$$\left\langle \sum_{j=1}^{N}\int_0^1 \mathrm{d}s \exp\left(\mathrm{i}\mathbf{q}\cdot\mathbf{c}_j(s,0)\right) \exp\left(-\mathrm{i}\mathbf{q}\cdot\mathbf{c}_j(s,t)\right)\right\rangle_\chi, \quad (1.2)$$

where $\mathbf{c}_j(s,t)$ is the position of the monomer at time t, the $t \to \infty$ limit of the correlator being proportional (up to disorder averaging) to a special case of equation (1.1), *viz.*,

$$\frac{1}{N}\sum_{j=1}^{N}\int_0^1 \mathrm{d}s \left\langle \exp \mathrm{i}\mathbf{q}\cdot\mathbf{c}_j(s)\right\rangle_\chi \left\langle \exp -\mathrm{i}\mathbf{q}\cdot\mathbf{c}_j(s)\right\rangle_\chi . \quad (1.3)$$

On the other hand, in several other experimental techniques, such as those discussed below, it is some form of correlator involving the local monomer density

$$\rho(\mathbf{r},t) \equiv \sum_{j=1}^{N}\int_0^1 \mathrm{d}s\, \delta(\mathbf{r}-\mathbf{c}_j(s,t)) \quad (1.4)$$

that is probed. One frequently-measured correlator is the auto-correlation function of the local density $\langle \rho(\mathbf{x},0)\,\rho(\mathbf{y},t)\rangle_\chi$, or equivalently $\langle \rho(\mathbf{q},0)\rho(-\mathbf{q},t)\rangle_\chi$, where $\rho(\mathbf{q})$ is the Fourier transform of $\rho(\mathbf{x})$, *i.e.*, $\rho(\mathbf{q}) = \int \mathrm{d}^d x\, \rho(\mathbf{x}) \exp(-\mathrm{i}\mathbf{q}\cdot\mathbf{x})$ [12]. For example, in neutron scattering experiments this quantity is proportional to the *coherent* part of the quasi-elastic neutron scattering cross-section (see, *e.g.*, Ref. [4], Sect. IIIE), and in dynamical light scattering experiments, such as those performed on 'non-ergodic' media by Pusey and van Megen [7], this quantity is proportional to the intermediate scattering function (also known as the dynamical structure factor) $F(k,t)$. (The average over quenched disorder $[\cdots]$ in the present work essentially plays the role of the ensemble average $\langle \cdots \rangle_{\mathrm{E}}$ of Ref. [7].) The present theoretical framework is a static equilibrium framework and, as such, is not suitable for computing dynamical correlators. However, by using the cluster property (*i.e.* the fact that the connected correlators vanish for $t \to \infty$) we see that the long-time limit of the density-density auto-correlation function is built from the equilibrium entity $\langle \rho(\mathbf{x})\rangle_\chi \langle \rho(\mathbf{y})\rangle_\chi$ or, equivalently, its Fourier transform $\langle \rho(\mathbf{q})\rangle_\chi \langle \rho(-\mathbf{q})\rangle_\chi$, an entity that is calculable (up to disorder averaging) within our static equilibrium framework. In fact, our approach to the VT is capable of calculating precisely this kind of quantity and, therefore, of providing contact with experiments.

As our results for density correlators are relatively straightforward, we first report the results, deferring the construction and operation of the necessary theoretical machinery to subsequent sections. Specifically, we find that:

(i) The usual (*i.e.* disorder-averaged) density-density correlator $[\langle \rho(\mathbf{q})\rho(-\mathbf{q})\rangle_\chi]$ is insensitive to the VT, depending only analytically on the constraint density, both at the level of mean-field theory and beyond (*i.e.* to one-loop order).

(ii) The density-density correlator involving two thermal averages, $[\langle \rho(\mathbf{q})\rangle_\chi \langle \rho(-\mathbf{q})\rangle_\chi]$, is zero in the liquid phase but becomes nonzero, continuously, as the system enters the amorphous solid phase. This behavior is a manifestation of the freezing-in of random density fluctuations, which is the hallmark of the amorphous solid state. This correlator turns out to be proportional to the order parameter (at least for weak coupling between the density and the order parameter fluctuations). As the order parameter encodes the fraction of localized particles and the distribution of localization lengths, this result indicates that these physical diagnostics are accessible *via* this density-density correlator.

(iii) The four-density correlator involving two thermal averages, $[\langle \rho(\mathbf{k})\rho(-\mathbf{k})\rangle_\chi \langle \rho(\mathbf{q})\rho(-\mathbf{q})\rangle_\chi]$, which can be realized as $\lim_{t\to\infty}[\langle \rho(\mathbf{k},0)\rho(-\mathbf{k},0)\rho(\mathbf{q},t)\,\rho(-\mathbf{q},t)\rangle_\chi]$, becomes long-ranged as the VT is approached from the liquid side. We exhibit this phenomenon at the level of mean-field theory.

(iv) The two density-channel signatures of the VT given in (ii) and (iii) also provide a means for identifying certain critical exponents at the VT, such as the gel-fraction exponent β, and the correlation-length exponent ν. Therefore, these density signatures provide another avenue for accessing experimentally the critical exponents of the VT.

2 Field-theoretic formulation: Minimal model and coupling to density field

We approach the VT by adopting the spirit of the Landau-Wilson scheme for continuous phase transitions.

To handle the presence of the random constraints we invoke the replica trick and adopt the Deam and Edwards model [13] for the statistics of the quenched randomness (*viz.* that the statistics of the random constraints are determined by the instantaneous correlations of the unconstrained system). Thus, we are led to the need to work with the $n \to 0$ limit of systems of $n+1$ replicas. The additional replica, labeled by $\alpha = 0$, incorporates the constraint distribution. With the effective spatial dimensionality thus being determined to be $(n+1)d$, symmetry considerations lead to the following minimal model [5], which takes the form of a cubic field theory involving an order parameter field $\Omega(\hat{k})$ that lives on $(n+1)$-fold replicated d-dimensional space [14]:

$$f \propto -\lim_{n\to 0} n^{-1} \ln[Z^n] \,, \tag{2.1a}$$

$$[Z^n] \propto \int \overline{\mathcal{D}}^{\dagger}\, \Omega \exp(-\mathcal{F}_n^{\mathrm{HRS}}), \tag{2.1b}$$

$$\mathcal{F}_n^{\mathrm{HRS}}(\Omega) = N \sum_{\hat{k}\in\mathrm{HRS}} \Big(-a\tau + \frac{b}{2}|\hat{k}|^2 \Big) \big|\Omega(\hat{k})\big|^2 - Ng \times \sum_{\hat{k}_1,\hat{k}_2,\hat{k}_3\in\mathrm{HRS}} \Omega(\hat{k}_1)\,\Omega(\hat{k}_2)\,\Omega(\hat{k}_3)\,\delta_{\hat{k}_1+\hat{k}_2+\hat{k}_3,\hat{0}}. \tag{2.1c}$$

Here, τ is the VT control parameter, which measures the reduced density of random constraints, and the coefficients a, b and g depend on the microscopic details of the system. We use the symbol $\hat{k}$ to denote the replicated wavevector $\{\mathbf{k}^0, \mathbf{k}^1, \ldots, \mathbf{k}^n\}$, and define the extended scalar product $\hat{k}\cdot\hat{c}$ by $\mathbf{k}^0\cdot\mathbf{c}^0 + \mathbf{k}^1\cdot\mathbf{c}^1 + \cdots + \mathbf{k}^n\cdot\mathbf{c}^n$. The symbol $\hat{k}\in\mathrm{HRS}$ denotes that the summation over replicated wavevectors is restricted to those containing at least two nonzero component-vectors $\mathbf{k}^\alpha$. (We say that this kind of wavevector lies in the higher-replica-sector, *i.e.*, the HRS.) This condition on $\hat{k}$ reflects the fact that no crystalline order (or any other kind of macroscopic inhomogeneity) is present or fluctuates critically in the vicinity of the VT. In addition to symmetry considerations, the minimal model exhibited in Eq. (2.1c) can be derived from a semi-microscopic model. (For a detailed review of the semi-microscopic model, see Ref. [4].) In the approach based on such a model, one can demonstrate that the order parameter shown in equation (1.1) is provided by $\langle\Omega(\hat{k})\rangle^{\mathcal{F}_n^{\mathrm{HRS}}}|_{n\to 0}$, where $\langle\cdots\rangle^{\mathcal{F}_n^{\mathrm{HRS}}}$ denotes a statistical average weighted by $\mathcal{F}_n^{\mathrm{HRS}}$, if one makes the choice $\hat{k} = \{\mathbf{0}, \mathbf{k}^1, \mathbf{k}^2, \ldots, \mathbf{k}^A, \mathbf{0}, \ldots, \mathbf{0}\}$.

We now extend the effective free energy, equation (2.1c), by including the field R that is associated with spatial monomer density fluctuations, *i.e.*, $R = \sum_{j=1}^N \int_0^1 \mathrm{d}s\, \exp \mathrm{i}\mathbf{k}\cdot\mathbf{c}_j(s)$ [15]. The field R takes as its argument replicated wavevectors having exactly one nonzero component-vector $\mathbf{k}\hat{e}^\alpha$. (We denote by $\{\hat{e}^\alpha\}_{\alpha=0}^n$ the collection of unit vectors in replicated space, so that, *e.g.*, a generic replicated vector $\hat{p}$ can be expressed as $\sum_{\alpha=0}^n \mathbf{p}^\alpha\hat{e}^\alpha$.) We term the subset of replicated wavevectors having exactly one nonzero component-vector the one-replica-sector (1RS) of wavevectors; we term the corresponding fields $R(\mathbf{k}\hat{e}^\alpha)$ 1RS fields. We extend the effective Landau free energy, equation (2.1c), by incorporating the 1RS fields $R(\mathbf{k}\hat{e}^\alpha)$ [16], which represent local density fluctuations, and add the significant symmetry-allowed cubic term that couples the order-parameter and density fields, thus arriving at

$$\mathcal{F}_n(\Omega, R) = \mathcal{F}_n^{\mathrm{HRS}}(\Omega) + \mathcal{F}_n^{\mathrm{1RS}}(R) - \frac{h}{N} \sum_{\substack{\hat{k}_3\in\mathrm{HRS}\\ \hat{k}_1,\hat{k}_2\in\mathrm{1RS}}} R(\hat{k}_1)\,R(\hat{k}_2)\,\Omega(\hat{k}_3)\,\delta_{\hat{k}_1+\hat{k}_2+\hat{k}_3,\hat{0}}\,, \tag{2.2a}$$

$$\mathcal{F}_n^{\mathrm{1RS}}(R) = \frac{1}{N}\sum_{\hat{k}\in\mathrm{1RS}} \Big(r^{-2} + \frac{c}{2}|\hat{k}|^2 \Big) \big|R(\hat{k})\big|^2 + \cdots \tag{2.2b}$$

The term $\mathcal{F}_n^{\mathrm{1RS}}(R)$ is the effective free energy for the density fluctuations; in principle, it also includes non-linear couplings between the R fields. This effective free energy term already incorporates the effects of the short-range repulsion between macromolecules. The parameter r is the correlation length for density fluctuations. (In the context of a dense melt, it is simply determined by the monomer density and the effective excluded-volume interaction strength [17].) The correlation length r remains large and varies analytically (with the constraint density) across the VT, and the R field remains a non-ordered field. This is representative of the fact that the *disorder-averaged* physical monomer-density is homogeneous in both the liquid state and the amorphous solid state.

In addition to the coupling presented in equation (2.2a), there is one further term at cubic order that couples the R and Ω fields, *i.e.*, the vertex $\Omega\Omega R$ consisting of two HRS fields and one 1RS field. It can readily be shown by dimensional analysis that both this cubic vertex and that given in equation (2.2a) are irrelevant with respect to the fixed points of HRS Ω theory near $d = 6$ and, therefore, the critical properties of the VT (*i.e.* the fixed point structure, the flow equation and the critical exponents) are not affected by the coupling to density fluctuations(at least near $d = 6$). Based on the effective free energy (2.2a), our approach is to explore the correlators of the 1RS fields (and hence the density correlators), taking into account the effects of the VT in the HRS fields by treating what happens in the HRS as "input" to be added to the effective free energy of the 1RS theory, and working perturbatively (*i.e.* effectively we assume that h is small).

The reason that we ignore the the cubic coupling $\Omega\Omega R$, besides its irrelevance in the renormalization-group sense, is that it does not contribute to the density correlators that we are interested in (at least to one-loop order). There are two points to make in this regard. First, at the mean-field level, the HRS field can be viewed as an external source for the 1RS field in the cubic coupling $\Omega\Omega R$. Due to translational invariance, $\langle\Omega(\hat{k}_1)\Omega(\hat{k}_2)\rangle^{\mathcal{F}_n^{\mathrm{HRS}}} = 0$. Therefore, on average, the term $\Omega\Omega R$ will not generate a non-zero $\langle R\rangle$ [$\langle\cdots\rangle$ denotes an average weighted by the replicated effective free energy presented in equation (2.2a)]. Second, at the one-loop level (and beyond),

$$\lim_{n\to 0}\left\langle R(\mathbf{k}\hat{e}^{\alpha})\,R(-\mathbf{k}\hat{e}^{\beta})\right\rangle = \begin{cases} \dfrac{N}{2r^{-2}+ck^2}, & \text{for } \alpha=\beta; \\ \dfrac{1}{2}\dfrac{Nh\overline{\Omega}(-\mathbf{k}\hat{e}^1+\mathbf{k}\hat{e}^2)}{(r^{-2}+\frac{1}{2}ck^2)((r^{-2}+\frac{1}{2}ck^2)+h\overline{\Omega}(-\mathbf{k}\hat{e}^1+\mathbf{k}\hat{e}^2))}, & \text{for } \alpha\neq\beta. \end{cases} \tag{3.3}$$

$$\left[\,\langle\rho(\mathbf{k})\rangle_{\chi}\,\langle\rho(-\mathbf{k})\rangle_{\chi}\,\right] = \begin{cases} 0, & \text{liquid state;} \\ (Nhr^4/2)\overline{\Omega}(-\mathbf{k}\hat{e}^1+\mathbf{k}\hat{e}^2) = (Nhr^4/2)\tau^{\beta}\,w(k^2\tau^{-2\nu}), & \text{amorphous solid state.} \end{cases} \tag{3.4}$$

this term will renormalize the coefficient r^{-2} (in a singular way) but, as has already been shown in Appendix B of reference [6], at least to the one-loop level, there is (in the replica limit) no contribution to the density-density correlator coming from HRS critical fluctuations *via* this kind of vertex.

In order to help make the physical content of the results that we shall present clear, we pause to give the relationship between the physical density correlators and the R correlators:

$$\lim_{n\to 0}\left\langle R(\mathbf{k}\hat{e}^{\alpha})\,R(-\mathbf{k}\hat{e}^{\beta})\right\rangle_{\mathrm{c}} = \begin{cases} \left[\langle\rho(\mathbf{k})\,\rho(-\mathbf{k})\rangle_{\chi}\right]; & \text{for } \alpha=\beta, \\ \left[\,\langle\rho(\mathbf{k})\rangle_{\chi}\,\langle\rho(-\mathbf{k})\rangle_{\chi}\,\right]; & \text{for } \alpha\neq\beta, \end{cases} \tag{2.3}$$

where c denotes that a correlator is connected. (Such connections can be established by following the replica technique that is used in Appendix A of Ref. [4].) On the right hand side of equation (2.3), the correlators differ in the locations of the thermal averages; on the left hand side they differ in their replica indices, the former being diagonal and the latter being off-diagonal in replica space.

3 Freezing-in of density fluctuations

Now that we have constructed an extended model containing not only the critical order parameter (*i.e.* HRS) fields but also the noncritical replicated density (*i.e.* 1RS) fields, we proceed to study the effect of critical HRS phenomena on the density fields, treating the latter at the tree level. The basic mechanism at work is that the order parameter field, which is capable of ordering spontaneously, couples to the density fluctuations *via* a cubic vertex that is replica-off-diagonal as far as the density fields are concerned. A non-zero value of $\overline{\Omega}\equiv\langle\Omega\rangle^{\mathcal{F}_n^{\mathrm{HRS}}}$, as occurs in the amorphous solid state due to spontaneous symmetry breaking in the HRS, contributes replica-off-diagonal terms to the "mass matrix" of the R-field and, hence, leads to the existence of nonzero replica-off-diagonal density-field correlators.

In order to see this more clearly, we replace Ω by its expectation value plus fluctuations, *i.e.*, we write $\Omega = \overline{\Omega}+\delta\Omega$ and, hence, arrive at the effective free energy

$$\mathcal{F}_n\big(R,\Omega\big) = \mathcal{F}_n^{\mathrm{HRS}}\big(\Omega\big) + \tilde{\mathcal{F}}_n^{\mathrm{1RS}}\big(R,\overline{\Omega}\big) - \tfrac{h}{N}\sum_{\substack{\hat{k}_3\in\mathrm{HRS}\\ \hat{k}_1,\hat{k}_2\in\mathrm{1RS}}} R(\hat{k}_1)\,R(\hat{k}_2)\,\delta\Omega(\hat{k}_3)\,\delta_{\hat{k}_1+\hat{k}_2+\hat{k}_3,\hat{0}}\,, \tag{3.1a}$$

$$\tilde{\mathcal{F}}_n^{\mathrm{1RS}}\big(R,\overline{\Omega}\big) = \tfrac{1}{N}\sum_{\mathbf{k}\neq\mathbf{0}}\sum_{\alpha,\beta=0}^{n}\big((r^{-2}+\tfrac{c}{2}k^2)\delta^{\alpha,\beta} - h\,\overline{\Omega}(-\mathbf{k}\hat{e}^1+\mathbf{k}\hat{e}^2)(1-\delta^{\alpha,\beta})\big)\,R(\mathbf{k}\hat{e}^{\alpha})R(-\mathbf{k}\hat{e}^{\beta}) + \cdots \tag{3.1b}$$

To arrive at this result, we have taken advantage of the facts that both $\mathcal{F}_n$ and $\overline{\Omega}$ are replica (*i.e.* permutation) symmetric, and that $\overline{\Omega}(-\mathbf{k}_1\hat{e}^{\alpha}-\mathbf{k}_2\hat{e}^{\beta})$ is macroscopically translational invariant (*i.e.* it contains a factor of $\delta_{\mathbf{k}_1+\mathbf{k}_2,\mathbf{0}}$) [5].

We now aim to compute the correlator $\left\langle R(\mathbf{k}\hat{e}^{\alpha})\,R(-\mathbf{k}\hat{e}^{\beta})\right\rangle$. By treating h as a small quantity and expanding perturbatively, a direct calculation yields

$$\left\langle R(\mathbf{k}\hat{e}^{\alpha})\,R(-\mathbf{k}\hat{e}^{\beta})\right\rangle = \left\langle R(\mathbf{k}\hat{e}^{\alpha})\,R(-\mathbf{k}\hat{e}^{\beta})\right\rangle^{\tilde{\mathcal{F}}_n^{\mathrm{1RS}}} + O(h^2). \tag{3.2}$$

To obtain the correlator at the tree (in R) level, we neglect the nonlinear self-couplings of R and then invert the coefficient matrix of the quadratic term in equation (3.1b). Thus, in the $n\to 0$ limit, we arrive at

See equation (3.3) above.

In the liquid state we have $\overline{\Omega}=0$, and therefore $\langle R(\mathbf{k}\hat{e}^{\alpha})\,R(-\mathbf{k}\hat{e}^{\beta})\rangle = 0$ (for $\alpha\neq\beta$). However, in the amorphous solid state $\overline{\Omega}(\mathbf{k}_1\hat{e}^1+\mathbf{k}_2\hat{e}^2) = q\delta_{\mathbf{k}_1+\mathbf{k}_2,\mathbf{0}}\,w(k_1^2+k_2^2)\neq 0$, and therefore $\langle R(\mathbf{k}\hat{e}^{\alpha})\,R(-\mathbf{k}\hat{e}^{\beta})\rangle\neq 0$ (for $\alpha\neq\beta$). Here, the number q is the gel fraction and the function $w(|\hat{k}|^2)$, which decays rapidly with increasing wavevector magnitude on the characteristic wavevector scale τ^{ν} [6], encodes the distribution of localization lengths. The simplest setting for the density-density correlator emerges near the VT, where q is small and $w(|\hat{k}|^2)$ is negligible unless $|\hat{k}|\lesssim\tau^{\nu}$. In this regime, by making use of equation (2.3) we find that

See equation (3.4) above.

On the other hand, the diagonal correlator $\left[\,\langle\rho(\mathbf{k})\rho(-\mathbf{k})\rangle_{\chi}\,\right]$ does not vary with τ (and hence varies smoothly with the physical constraint density).

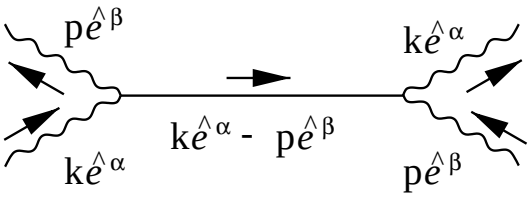

Fig. 1. Divergent 4-field tree level density correlator. Solid line indicates the bare HRS correlator; wavy lines indicate bare 1RS correlators.

Deeper into the amorphous solid state, the order parameter $\overline{\Omega}$ does not decay so rapidly with k and hence the quantity $\left[\ \langle\rho(\mathbf{k})\rangle_\chi\ \langle\rho(-\mathbf{k})\rangle_\chi\ \right]$ should remain appreciable (and thus experimentally accessible) over a wider range of k. Now, we expect equation (3.3) to remain valid, provided the coupling h is small and both the wavevector dependence of h and the finer wavevector dependence of 1RS bare correlator are incorporated. (We have omitted the wavevector dependence of h so as to simplify our presentation.) Under these circumstances, the wavevector dependence of the replica-off-diagonal correlator has the possibility of exhibiting additional features, representative of the ordinary density-density correlator $\left[\left\langle\rho(\mathbf{k})\rho(-\mathbf{k})\right\rangle_\chi\right]$, superposed on the decaying trend due to the factor w (*i.e.* due to random monomer localization) [19].

4 Inherited criticality of density correlators

In the HRS field theory, the VT is signaled in two ways: (i) *via* the emergence of a nonzero order parameter, and (ii) *via* the divergence of the correlation length of order-parameter fluctuations. We have already studied the replica-off-diagonal density correlator, which is closely related to the order parameter and becomes nonzero upon entering the amorphous solid state. We now examine the four-field density correlator $[\langle\rho(\mathbf{k})\,\rho(-\mathbf{k})\rangle_\chi\,\langle\rho(\mathbf{p})\,\rho(-\mathbf{p})\rangle_\chi]$, which has the property that it becomes long-ranged at the VT.

We calculate the correlator mentioned in the previous sentence at the tree level (with respect to h vertices) in the liquid state and at the VT itself: the Feynman diagram shown in Figure 1 is the only contribution, and gives

$$\begin{aligned}
&[\langle\rho(\mathbf{k})\,\rho(-\mathbf{k})\rangle_\chi\,\langle\rho(\mathbf{p})\,\rho(-\mathbf{p})\rangle_\chi] \\
&\quad= \lim_{n\to 0}\langle R(\mathbf{k}\hat{e}^\alpha)R(-\mathbf{p}\hat{e}^\beta)R(-\mathbf{k}\hat{e}^\alpha)R(\mathbf{p}\hat{e}^\beta)\rangle \\
&\quad\propto (h/N)^2\Big\{\langle R(\mathbf{k}\hat{e}^\alpha)R(-\mathbf{k}\hat{e}^\alpha)\rangle^{\mathcal{F}_n^{\mathrm{1RS}}}\Big\}^2 \\
&\qquad\times\Big\{\langle R(\mathbf{p}\hat{e}^\beta)R(-\mathbf{p}\hat{e}^\beta)\rangle^{\mathcal{F}_n^{\mathrm{1RS}}}\Big\}^2 \\
&\qquad\times\langle\Omega(\mathbf{k}\hat{e}^\alpha-\mathbf{p}\hat{e}^\beta)\Omega(-\mathbf{k}\hat{e}^\alpha+\mathbf{p}\hat{e}^\beta)\rangle^{\mathcal{F}_n^{\mathrm{HRS}}}. \qquad (4.1)
\end{aligned}$$

As anticipated, this density correlator becomes long-ranged at the VT, due to the factor of the HRS order-parameter correlator $\langle\Omega\Omega\rangle^{\mathcal{F}_n^{\mathrm{HRS}}}$ which, itself, becomes long-ranged at the VT.

5 Discussion and conclusions

We have studied density-sector correlators that furnish analogs of the two principal order-parameter signatures of the VT: the off-diagonal density correlator $[\langle\rho(\mathbf{q})\rangle_\chi\,\langle\rho(-\mathbf{q})\rangle_\chi]$, which becomes nonzero as the amorphous solid state is entered; and the four-field density correlator $[\langle\rho(\mathbf{k})\,\rho(-\mathbf{k})\rangle_\chi\,\langle\rho(\mathbf{p})\,\rho(-\mathbf{p})\rangle_\chi]$, which becomes long-ranged at the VT. We have shown that these density correlators provide useful information about both the emergent amorphous solid state and the critical properties of the transition itself. They provide schemes for accessing experimentally the kinds of quantities that have been found useful in theoretical investigations of the liquid, critical and amorphous solid states, *e.g.*, of vulcanized matter. We are not aware of any explorations of such signatures in the density correlators *via* percolation/gelation approaches to the VT.

Although, as we have seen, the off-diagonal density correlator $[\langle\rho(\mathbf{q})\rangle_\chi\,\langle\rho(-\mathbf{q})\rangle_\chi]$ is closely related to the order parameter of the VT, its non-zero value being induced by a non-zero order parameter, the off-diagonal density correlator can be used to diagnose a more general class of systems. By looking at the microscopic definition of the order parameter for the VT, equation (1.1) (especially for the special case in which only two thermal averages are involved), we see that it involves only a *single* summation over monomers and, therefore, the order parameter cannot be expressed in terms of local monomer densities. In essence, the order parameter signals the amorphous solid phase *via* its detection of all individual monomers that are localized (and, owing to the explicit crosslinks, distinguishable). On the other hand, the off-diagonal density correlator $[\langle\rho(\mathbf{q})\rangle_\chi\,\langle\rho(-\mathbf{q})\rangle_\chi]$ signals the amorphous solid state *via* the detection of the frozen structure of the local density fluctuations. In RCMSs, the localization of monomers invariably induces the freezing of this structure, so these two quantities are equivalent. However in systems such as glasses, the (local density) structure is, presumably, frozen but each individual particle is able to wander throughout the system, given enough time, and therefore all particles retain their indistinguishability [18]. A quantity essentially identical to the off-diagonal correlator considered here has been employed by Mezard and Parisi [8] in the context of their theoretical approach to glassy systems. A similar quantity is employed in the diagnosis of the freezing-in of structure in colloidal glassy systems and gel systems in the dynamical light scattering experiments of Pusey and Van Megen and collaborators [7,20]

Vulcanized matter certainly differs from glassy systems, inasmuch as it possesses explicit quenched disorder in the form of permanent random crosslinks. Because of this, it affords a framework in which the off-diagonal density correlator and other density correlators are directly calculable in a well controlled way, both near the transition and in the amorphous solid state. Despite the difference with glassy systems, we hope that results such as those presented here in the setting of vulcanized matter will not only be useful but also shed some light on the more difficult problem of glassy systems.

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11. See, *e.g.*, D. Stauffer, A. Coniglio, M. Adam, Adv. in Polym. Sci. **44**, 103 (1982); T.C. Lubensky, J. Isaacson, Phys. Rev. Lett. **41**, 829 (1978).
12. Unless noted otherwise, the wavevector $\mathbf{q}$ is assumed to be non-zero.
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14. The measure $\overline{\mathcal{D}}^{\dagger}\Omega$ indicates that we integrate $\Omega(\hat{k})$ with $\hat{k} \in$ HRS and with $\hat{k}$ restricted to a half-space *via* an additional condition $\hat{k}\cdot\hat{m} > 0$ for some suitable unit $(n+1)d$-vector $\hat{m}$. This is due to the fact that $Q(-\hat{k}) = Q(\hat{k})^*$ (*i.e.* its Fourier transform is real).
15. We are departing from the convention of our previous works in order to avoid some unnecessary complications. Let us pause to clarify the relationship between these conventions. Here, we employ $R(\mathbf{k}\hat{e}^{\alpha})$ as our 1RS field variable, rather than the $\Omega(\mathbf{k}\hat{e}^{\alpha})$ used in references [4,6]. R is closely related to the variable Q that is microscopically defined in references [4,6]. In fact, $R(\mathbf{k}\hat{e}^{\alpha}) = NQ(\mathbf{k}\hat{e}^{\alpha}) = \sum_{j=1}^{N}\int_0^1 \mathrm{d}s\, \exp \mathrm{i}\mathbf{k}\cdot\mathbf{c}_j(s)$ [4]. The reason we choose $R(\mathbf{k}\hat{e}^{\alpha})$ instead of $\Omega(\mathbf{k}\hat{e}^{\alpha})$ is that the RR correlator is simply the density correlator as exhibited in equation (2.3), whereas the $\Omega\Omega$ correlator has a more complicated (and model dependent) relationship with the physical density correlator because $\Omega(\mathbf{k}\hat{e}^{\alpha})$ is a conjugate variable resulting from a Hubbard-Stratonovich transformation of $Q(\mathbf{k}\hat{e}^{\alpha})$. In order to avoid this unnecessary complication, we adopt the $R(\mathbf{k}\hat{e}^{\alpha})$ as our field variable. In principle, one can construct such a minimal model by following the general symmetry considerations that lead to the minimal model for $\Omega(\hat{k})$.
16. Functional integration over 1RS fields is implied.
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