


Configurational entropy from a replica approach: A density-functional model

Prakash Vardhan and Shankar P. Das 

School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India



(Received 17 December 2020; accepted 18 January 2022; published 8 February 2022)

We study a field-theoretic model for the metastable liquid using a nonlocal free-energy functional with density $\rho(\mathbf{x})$ as the order parameter and three-point correlation effects included in the formulation. We assume fragmentation of the free-energy landscape into distinct basins of local minima and evaluate the partition function for the many-particle system through mapping into a composite system of m identical replicas. Static correlations and configurational entropy \mathcal{S}_c are calculated in the $m = 1$ limit. The Kauzmann packing fraction η_K obtained are in agreement with other works.

DOI: [10.1103/PhysRevE.105.024110](https://doi.org/10.1103/PhysRevE.105.024110)

I. INTRODUCTION

The liquid remains disordered well below its crystallization point and becomes metastable with respect to the ordered crystalline state. Understanding how the metastable liquid transforms into an amorphous solid [1] having rigidity has remained a challenge. The concepts of ergodicity breaking and the associated entropy crisis are essential tools for building a microscopic model for this process. The density $\rho(\mathbf{x})$ is treated as the order parameter field in these theoretical descriptions. A typical example is the classical density-functional theory (DFT) used to understand crystallization. In DFT, the inhomogeneous density $\rho(\mathbf{x})$ is treated as the order parameter and the equilibrium state is identified by minimizing a suitable free-energy functional. The free energy for the normal liquid state corresponds to the global minimum of this functional corresponding to a uniform density $\rho(\mathbf{x}) = \rho_0$. Extending similar ideas [2,3], the metastable liquid below the freezing point is identified to be at a local minimum in the free-energy landscape (FEL). With the increase of density, the FEL breaks up into an exponentially large number of basins corresponding to local minima of the free-energy functional, signifying the metastable amorphous states. This transformation of the metastable liquid is termed the spontaneous breakdown of ergodicity [1]. The metastable system can remain in a basin α characterized by a local minimum f_α (say) for the free energy. In a statistical mechanical description of the classical N -particle system, the partition function \mathcal{Z}_N is obtained by summing the contributions from the Boltzmann factors corresponding to these different basins $\{f_\alpha\}$,

$$\mathcal{Z}_N \simeq \sum_{\alpha} \int_{x \in \alpha} dx e^{-\beta H(x)} = \sum_{\alpha} e^{-\beta N f_\alpha(T)}. \quad (1)$$

\mathcal{H} denotes the microscopic Hamiltonian as a function of phase-space variables x and $\beta = 1/(k_B T)$ is the inverse temperature. The Boltzmann factors corresponding to a specific basin are shown on the right-hand side of Eq. (1) include

two types of contributions. First, the Boltzmann weight corresponds to the system being confined to a particular basin and, second, contributions arising from the different states corresponding to a given basin. The latter is referred to as vibrational contributions in that particular basin. In an idealized situation, the system is confined in a given basin in the FEL, vibrating around the corresponding minimum. This confinement requires infinite barriers between different states such that the system is confined in a single basin. In mean-field p -spin models in which every spin interacts with every other spin, this is a more appropriate situation [4,5]. In the present context, we focus on the primary contribution coming from the minimum of a given basin and consider the following scenario for the evolution of the FEL. Above the freezing point, the significant contribution to \mathcal{Z}_N comes from only one global minimum signifying the homogeneous liquid state with uniform density. Close to the freezing point, an exponentially large number of metastable states with free energies higher than that for the uniform state appear. However, these metastable states do not contribute to the Gibbs partition function since their numbers do not compensate for their small Boltzmann weight compared to that coming from the global minimum. At some lower temperature or higher packing, the number of metastable states becomes large enough to make up for the difference and contribute to the partition function. Below the freezing point, we obtain the partition function \mathcal{Z}_N for the system without any quenched disorder in terms of the contributions from these metastable states following the approximation in the right-hand side of Eq. (1)

In a field-theoretic description of the coarse-grained system in terms of a field $\phi(\mathbf{x})$, we obtain the partition function $\mathcal{Z}_N[\phi]$ in terms of the corresponding Hamiltonian $\mathcal{H}[\phi]$ as

$$\mathcal{Z}_N = \int \mathcal{D}\phi(x) \exp\{-\beta \mathcal{H}[\phi]\}. \quad (2)$$

The state of the many-particle systems representing a liquid matter is described in terms of the free-energy functional

value in the function space of a continuum field. We identify this field here with the coarse-grained density function $\rho(\mathbf{x})$ [6]. In the classical DFT the inhomogeneous function $\rho(\mathbf{x})$ is treated as an order parameter. The equilibrium state of the many-particle system is identified by minimizing a suitable functional $\mathcal{H}[\rho(\mathbf{x})]$. Local minima of $\mathcal{H}[\rho]$ in space of $\rho(\mathbf{x})$ signify the metastable basins $\{f_\alpha\}$ depicted above. An essential step in developing the theoretical models to identify the local minima came from Ref. [6]. In this work, the metastable liquid was identified with local minima of free energy by imposing a δ -function constraint, $\delta(\delta\mathcal{H}/\delta\rho)$, in the calculation of \mathcal{Z}_N . A conjugate hatted field $\hat{\rho}$ is introduced in an integral representation to maintain this δ function constraint. It is assumed here that a nonzero correlation between the fields ρ and $\hat{\rho}$ signify ergodicity breaking [6]. The role of such auxiliary fields in picking up the local minima was further exploited in Monasson's seminal work [7], which we closely follow here in counting the number of local minima. An externally quenched pinning field $\psi(x)$ is coupled to $\rho(x)$ in the quadratic form in the corresponding free-energy functional $\mathcal{H}_\psi[\beta]$, such that when $\psi(x)$ is identical to $\rho(x)$ the corresponding \mathcal{H}_ψ is minimum by choice. The Monasson approach to accounting for the metastable minima involves using an ingenious trick of introducing m identical replica of the same system and then taking the physical limit $m \rightarrow 1$. The configurational entropy \mathcal{S}_c of the metastable liquid is calculated using this approach.

Configurational entropy for the metastable liquid has been defined in various ways, e.g., in terms of temperature derivatives of the free energy [8,9], in terms of local minima in the potential-energy landscape [10], using effective potential approximation for the self-generated disorder [11], and with a small cage expansion for individual particles vibrating around their mean positions of an amorphous structure [12]. In the description depicted above in terms of basins in the FEL, the logarithm of the number of such basins of free-energy minima at a given temperature obtains the corresponding configurational entropy or complexity \mathcal{S}_c of the supercooled liquid. In the deeply metastable state with its characteristic slow dynamics, \mathcal{S}_c decreases rapidly.

In the present work, using a density-functional representation of $\mathcal{H}[\rho]$, we include the effects of multiparticle correlations in the dense liquid in the calculation of the complexity \mathcal{S}_c . The partition function is evaluated from the sum on the right-hand side of Eq. (1) under spontaneous ergodicity breaking approximation. We obtain how \mathcal{S}_c drops with an increase of packing for a hard-sphere system, and by extrapolating \mathcal{S}_c to zero, the Kauzmann point [13] is estimated. The paper is organized as follows: The following section discusses the field-theoretic model for the structural system without quenched-disorder, using density as the order parameter. Section III presents the renormalization due to the coupling of density fluctuations beyond Gaussian order using standard methods. In Sec. IV, we present, following Monasson's approach, the scenario of spontaneous breaking of ergodicity in terms of nonzero correlations between identical replicas. Here we solve the corresponding equations for the nonergodicity parameters. In the next section, using the replica approach, we calculate the configurational entropy or complexity \mathcal{S}_c in terms of the number of local minima in the FEL. In Sec. VI

we consider the present model with respect to the ergodicity-nonergodicity transition of mode-coupling theory (MCT). We end the paper with a short discussion of the results.

II. THE FIELD-THEORETIC MODEL

In a continuum field-theoretic description, the minima corresponding to the different basins of the FEL are defined in terms of the function space of $\rho(x)$. The equilibrium free energy for the system is obtained as a functional integral over ρ ,

$$\mathcal{F}(\beta) = -\beta^{-1} \ln \int \mathcal{D}\rho(x) \exp\{-\beta\mathcal{H}[\rho]\}. \quad (3)$$

$\mathcal{H}[\rho]$ is the Hamiltonian expressed as a functional of continuum order parameter field $\rho(x)$ and $(\beta m_0)^{-1/2}$ is the average speed of the fluid particles of mass m_0 . The free-energy values at the bottom of the respective basins are picked up by introducing [6,7] an externally quenched pinning field $\psi(x)$ coupled to $\rho(x)$ with a coupling $g > 0$. The corresponding free energy is obtained as a generalization of Eq. (3):

$$\begin{aligned} \mathcal{F}_\psi[g, \beta] = & -\beta^{-1} \ln \int \mathcal{D}\rho(x) \\ & \times \exp \left\{ -\beta\mathcal{H}[\rho] - \frac{g}{2} \int dx [\psi(x) - \rho(x)]^2 \right\}. \end{aligned} \quad (4)$$

The free energy $\mathcal{F}_\psi[g, \beta]$ is minimum when the pinning field $\psi(x)$ is identical to $\rho(x)$ corresponding to the minima of unperturbed free energy given by Eq. (3). Therefore spanning the function space of $\psi(x)$ picks up in the partition function sum, the contribution from the respective minima corresponding to different basins in the FEL. For a chosen temperature $\tilde{\beta} = m\beta$ (for integer m), the corresponding partition function $\mathcal{W}(\tilde{\beta})$ of the original system is calculated by mapping into a composite system of m identical replicas. Performing a simple Gaussian integral, we obtain

$$\begin{aligned} e^{-\tilde{\beta}\mathcal{F}} \equiv \mathcal{W}(\tilde{\beta}) = & \lim_{g \rightarrow 0^+} \left[\int \prod_{a=1}^m \mathcal{D}\rho^a(x) \exp \left\{ -\beta \sum_{a=1}^m \mathcal{H}[\rho^a] \right. \right. \\ & \left. \left. - \frac{g}{2m} \sum_{a < b} \int \{\rho^a(x) - \rho^b(x)\}^2 dx \right\} \right]. \end{aligned} \quad (5)$$

The density field $\rho(\mathbf{x})$ for the composite system with the m replicas is denoted here as $\{\rho^a\} = \{\rho^1\}\{\rho^2\}\{\rho^3\} \dots \{\rho^m\}$. The internal energy $\mathcal{U}(\beta, m)$ for the system is obtained as

$$\mathcal{U}(\beta, m) = -\frac{\partial}{\partial \tilde{\beta}} \ln \mathcal{W}(\tilde{\beta}) = \frac{\partial}{\partial m} \{m\mathcal{F}[\beta, m]\}, \quad (6)$$

treating β as a constant. With the above scenario of the fragmented FEL having distinct basins, $\exp[\mathcal{S}_c]$ is counted for the number of local minima. For $m = 1$ the difference, $\beta(\mathcal{U} - \mathcal{F}) = \mathcal{S}_c$, obtains the configurational entropy of the metastable liquid. Using Eq. (6) obtains

$$\mathcal{S}_c = \beta \left[\frac{\partial}{\partial m} \mathcal{F}[\beta, m] \right]_{m=1}. \quad (7)$$

Following the DFT, we obtain the functional $\mathcal{H}[\rho(\mathbf{x})]$, in terms of which the partition function is formulated in Eq. (3),

in two parts,

$$\mathcal{H}[\rho] = \mathcal{H}_{\text{id}}[\rho] + \mathcal{H}_{\text{ex}}[\rho]. \quad (8)$$

The ideal gas or noninteracting part $\mathcal{H}_{\text{id}}[\rho]$ is obtained exactly as

$$\mathcal{H}_{\text{id}}[\rho] = \int d\mathbf{x} \rho(\mathbf{x}) [\ln(\rho(\mathbf{x})\Lambda^3) - 1], \quad (9)$$

$$\mathcal{H}_{\text{ex}}[\rho] = \mathcal{H}_{\text{ex}}^0 + \sum_{n=1}^{\infty} \frac{1}{n!} \int d\mathbf{x}_1 \dots d\mathbf{x}_n c^{(n)}(\mathbf{x}_1, \mathbf{x}_2, \dots) \delta\rho(\mathbf{x}_1) \dots \delta\rho(\mathbf{x}_n). \quad (10)$$

The direct correlation functions $c^{(n)}(\mathbf{x}_1, \mathbf{x}_2, \dots)$ s are functional derivatives of the excess free energy, i.e.,

$$c^{(n)}(\mathbf{x}_1, \mathbf{x}_2, \dots) = - \left. \frac{\delta^n \mathcal{H}_{\text{ex}}}{\delta\rho(\mathbf{x}_1) \dots \delta\rho(\mathbf{x}_n)} \right|_{\rho=\rho_0}. \quad (11)$$

Using translation symmetry, Fourier transform of $c^{(n)}$ is written in a dimensionless form with the symbol $\tilde{c}^{(n)} \equiv \rho_0^n c^{(n)}(\mathbf{k}_1, \dots, \mathbf{k}_n)$. Contributions from terms beyond cubic order in density fluctuations in the $\mathcal{H}[\rho]$ are ignored. The dominant contribution to the free energy comes from close to the local minima, and from physical considerations, these are finite. The present coarse-grained description of the fluid holds up to a cutoff length and restricts the wave vector range studied. With purely local Hamiltonian, it has been observed that the cubic term further strengthens the presence of the glassy state [14]. Keeping up to the cubic order terms in density fluctuations, the free-energy functional has the form,

$$\begin{aligned} \mathcal{H}[\rho(\mathbf{x})] = & \mathcal{H}(\rho_0) + \int \rho(\mathbf{x}_1) \left\{ \ln \left[\frac{\rho(\mathbf{x}_1)}{\rho_0} \right] - 1 \right\} d\mathbf{x}_1 \\ & - \frac{1}{2!} \int c^{(2)}(\mathbf{x}_1, \mathbf{x}_2) \delta\rho(\mathbf{x}_1) \delta\rho(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ & - \frac{1}{3!} \int c^{(3)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \delta\rho(\mathbf{x}_1) \\ & \times \delta\rho(\mathbf{x}_2) \delta\rho(\mathbf{x}_3) d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_3 + \dots \end{aligned} \quad (12)$$

Effects of the non-Gaussian terms are thus included in the calculation of correlation functions. Using the above form for $\mathcal{H}[\rho]$ for the composite system of m -identical replicas, free energy is written as a functional of the density fields of the various replicas. And these inter-replica fields couple beyond the Gaussian order.

III. RENORMALIZATION OF NON-GAUSSIAN MODEL

In the general formulation [15] of the field-theoretic model, the partition function \mathcal{W}_μ is obtained in terms of a functional integral over the field Ψ as:

$$\mathcal{W}_\mu = \int D\Psi \exp\{-\mathcal{H}_\mu[\Psi]\}. \quad (13)$$

$\mathcal{H}[\Psi]$ in the right-hand side is written in the unit of Boltzmann factor β . We adopt here a compact notation for the fields as $\Psi(1) \equiv \{\delta\rho^a(\mathbf{x})\}$, where a is the replica index ranging

where Λ is the thermal wavelength. In Eq. (9), we denote the position coordinate as \mathbf{x} signifying the spatial vector. The ideal gas part \mathcal{H}_{id} is an entropic contribution and is related to considerations of packing. The expression for \mathcal{H}_{id} shows that an inhomogeneous $\rho(\mathbf{x})$, signifying particle localization, has lower entropy compared to that for a uniform state. The excess or interaction contribution $\mathcal{H}_{\text{ex}}[\rho]$ is written in a functional Taylor series expansion of density fluctuation, $\delta\rho(\mathbf{x}) = \rho(\mathbf{x}) - \rho_0$, around its value $\mathcal{H}_{\text{ex}}^0$ for average density ρ_0 ,

from $a = 1$ to m , and 1 stands for the spatial point \mathbf{x}_1 , etc. The polynomial expansion form suitable for the diagrammatic corrections of field-theoretic models is obtained as

$$\begin{aligned} \mathcal{H}_\mu[\Psi] = & \frac{1}{2} \sum_{1,2} \mathcal{G}_0^{-1}(12) \Psi(1) \Psi(2) \\ & + \frac{1}{3} \sum_{1,2,3} V(123) \Psi(1) \Psi(2) \Psi(3) - \sum_1 \mu(1) \Psi(1). \end{aligned} \quad (14)$$

Here μ is the chemical potential. Using the DFT form for $\mathcal{H}[\rho]$ stated above in Eqs. (8)–(12), the zeroth order or Gaussian matrix, \mathcal{G}_0^{-1} is obtained as

$$\{\mathcal{G}_0^{-1}\}_{ab}(12) = \rho_0^{-1} [\delta(1-2) - \tilde{c}^{(2)}(12)] \delta_{ab}, \quad (15)$$

while the vertex function $V(123)$, taken to be the same for the identical replicas, are obtained as

$$\begin{aligned} V^{abc}(123) = & \rho_0^{-2} [\tilde{c}^{(3)}(123) + \delta(1-2)\delta(1-3)] \delta_{ab} \delta_{bc} \\ \equiv & V_0(123) \delta_{ab} \delta_{bc}. \end{aligned} \quad (16)$$

The vertices are chosen by construction to be symmetric in their arguments. The direct correlation functions $\tilde{c}^{(2)}$ and $\tilde{c}^{(3)}$ are respectively scaled with factors of ρ_0 and ρ_0^2 to make the corresponding Fourier transforms $\tilde{c}^{(2)}(k)$ and $\tilde{c}^{(3)}(\mathbf{k}, \mathbf{k}')$ dimensionless.

The two-point correlation matrix in the space of m identical replicas defined as

$$\mathcal{G}_{ab}(x-y) = \langle \delta\rho^a(x) \delta\rho^b(y) \rangle \quad (17)$$

is a key quantity here. Now taking a functional derivative of $\langle \Psi(1) \rangle = \mathcal{G}(1)$, with respect to $\mu(2)$, we obtain

$$\begin{aligned} \frac{\delta \mathcal{G}(1)}{\delta \mu(2)} = & \frac{\delta}{\delta \mu(2)} \int D\Psi \left[\frac{e^{-\mathcal{H}_\mu}}{\mathcal{W}_\mu} \right] \Psi(1) \\ = & \langle \Psi(1) \Psi(2) \rangle - \langle \Psi(1) \rangle \langle \Psi(2) \rangle \\ = & \langle \delta\Psi(1) \delta\Psi(2) \rangle \equiv \mathcal{G}(12). \end{aligned} \quad (18)$$

In the space of identical replicas, the correlation matrix \mathcal{G} is assumed to have the structure

$$\mathcal{G} = (G - F)\mathbf{I} + F\mathbf{E}. \quad (19)$$

\mathbf{I} is the $m \times m$ identity matrix, while \mathbf{E} is a matrix of the same size, having all the elements equal to unity. Renormalization of the Gaussian theory due to cubic and higher-order terms

[16] of the free energy is done using standard diagrammatic methods [15] of field theory. The renormalized two-point correlation function is obtained from the identity

$$\left\langle \int D\Psi \frac{\delta}{\delta\Psi_a(1)} \exp[-\mathcal{H}_\mu(\Psi)] \right\rangle = 0. \quad (20)$$

$$\{\mathcal{G}_0^{-1}\}_{\bar{a}\bar{b}}(1\bar{2})\langle\Psi^{\bar{b}}(\bar{2})\rangle + V^{\bar{a}\bar{b}\bar{c}}(1\bar{2}\bar{3})[\mathcal{G}_{\bar{b}\bar{c}}(\bar{2}\bar{3}) + \langle\Psi^{\bar{b}}(\bar{2})\rangle\langle\Psi^{\bar{c}}(\bar{3})\rangle] = \mu^{\bar{a}}(1). \quad (21)$$

We also use the fact that the three-point vertex function $V(123)$ is symmetric under the exchange of the indices. Taking one more derivative of Eq. (21) with respect to $\mu^{\bar{b}}(2)$, we obtain

$$\{\mathcal{G}_0^{-1}\}_{\bar{a}\bar{b}}(1\bar{2})\mathcal{G}_{\bar{b}\bar{b}}(\bar{2}2) + V^{\bar{a}\bar{b}\bar{c}}(1\bar{2}\bar{3})\left[\mathcal{G}_{\bar{b}\bar{b}}(\bar{2}2)\mathcal{G}_{\bar{c}}(\bar{3}) + \mathcal{G}_{\bar{b}}(\bar{2})\mathcal{G}_{\bar{c}\bar{b}}(\bar{3}2) + \frac{\delta\mathcal{G}_{\bar{b}\bar{c}}(\bar{2}\bar{3})}{\delta\mu^{\bar{b}}(2)}\right] = \delta(12)\delta_{\bar{a}\bar{b}}. \quad (22)$$

Now, taking a functional derivative (with respect to $\mu^{\bar{c}}$) of the following defining expression for the inverse of a matrix:

$$\mathcal{G}_{\bar{a}\bar{b}}^{-1}(1\bar{2})\mathcal{G}_{\bar{b}\bar{b}}(\bar{2}2) = \delta(12)\delta_{\bar{a}\bar{b}}, \quad (23)$$

the last term on right-hand side of Eq. (22) is obtained as

$$\frac{\delta\mathcal{G}_{\bar{a}\bar{c}}(13)}{\delta\mu^{\bar{b}}(2)} = -\mathcal{G}_{\bar{a}\bar{b}}(1\bar{2})\frac{\delta\mathcal{G}_{\bar{b}\bar{c}}^{-1}(\bar{2}\bar{3})}{\delta\mu^{\bar{b}}(2)}\mathcal{G}_{\bar{c}\bar{c}}(\bar{3}3). \quad (24)$$

Using the above identity (24) and some tedious algebra, the last terms on the right-hand side of Eq. (22) is further simplified. Introducing the self-energy matrix $\Sigma_{\bar{a}\bar{b}}$, we write Eq. (22) if the form

$$[\{\mathcal{G}_0^{-1}\}_{\bar{a}\bar{b}}(1\bar{2}) - \Sigma_{\bar{a}\bar{b}}(1\bar{2})]\mathcal{G}_{\bar{b}\bar{b}}(\bar{2}2) = \delta(12)\delta_{\bar{a}\bar{b}}. \quad (25)$$

In Appendix A, we have the following result for the self-energy matrix at lowest order in the bare vertex V ,

$$\Sigma_{\bar{a}\bar{b}}(12) = -2V^{\bar{a}\bar{b}\bar{c}}(1\bar{2}\bar{3})G_{\bar{c}}(\bar{3}) + 2V^{\bar{a}\bar{b}\bar{c}}(1\bar{2}\bar{3}) \times G_{\bar{b}\bar{d}}(\bar{2}\bar{4})G_{\bar{c}\bar{e}}(\bar{3}\bar{5})V^{\bar{d}\bar{e}\bar{b}}(\bar{4}\bar{5}2). \quad (26)$$

Using Eqs. (23) and (25), the inverse Green's function matrix \mathcal{G} is written in the form of Dyson's equation:

$$\mathcal{G}_{\bar{a}\bar{b}}^{-1}(12) = \{\mathcal{G}_0^{-1}\}_{\bar{a}\bar{b}}(12) - \Sigma_{\bar{a}\bar{b}}(12). \quad (27)$$

The self-energy matrix Σ represents the effects of the cubic and higher-order products of the fields Ψ in Eq. (14). Elements of Σ are obtained following diagrammatic methods [15] of field theory. For the isotropic system with constant μ , $\mathcal{G}_a(1) = \langle\Psi_a(1)\rangle = 0$ and hence the first term on the right-hand side of Eq. (26) is zero. In terms of the replica indices, the $\bar{a}\bar{b}$ element of the self-energy matrix Σ is obtained as

$$\Sigma_{\bar{a}\bar{b}}(12) = 2V_0(1\bar{2}\bar{3})G_{\bar{a}\bar{b}}(\bar{2}\bar{4})G_{\bar{a}\bar{b}}(\bar{3}\bar{5})V_0(\bar{4}\bar{5}2). \quad (28)$$

Note that in the right-hand side of Eq. (28) the repeated indices \bar{a} and \bar{b} are *not* summed over.

IV. THE SPONTANEOUS BREAKING OF ERGODICITY

Assuming that in the space of identical replicas, the self-energy matrix Σ has a structure similar to Eq. (19) with Σ_G

and Σ_F respectively denoting the diagonal and off-diagonal contributions,

$$\Sigma(12) = [\Sigma_G(12) - \Sigma_F(12)]\mathbf{I} + \Sigma_F(12)\mathbf{E}. \quad (29)$$

With this form, the Dyson equation (27) obtains

$$\mathcal{G}^{-1} = \{\mathcal{G}_0^{-1} + \Sigma_G - \Sigma_F\}\mathbf{I} + \Sigma_F\mathbf{E}. \quad (30)$$

Matrices of the above form are easily inverted, and \mathcal{G} reduces in the limit $m \rightarrow 1$ to the form (19) with the off-diagonal(diagonal) element obtained as $F(q)[G(q)]$. The following relations are obtained for F and G :

$$F(q) = G(q) - \Xi(q), \quad (31)$$

$$G^{-1}(q) = G_0^{-1}(q) - \Sigma_G(q), \quad (32)$$

$$\Xi^{-1}(q) = G^{-1}(q) + \Sigma_F(q). \quad (33)$$

In the liquid state, the off-diagonal elements $F(q)$ are zero. The diagonal elements $G(q)$, related to the static or thermodynamic properties, are not drastically affected through the ergodicity breaking transition. In the limit $g \rightarrow 0$, the contribution proportional to the coupling g in intrareplica $G(q)$ is negligible. For inter-replica $F(q)$, the same limit is nontrivial. It signals correlations developing in the replica space and the small extensive interaction between the identical copies or replicas force all the m replicas to fall in the same state, i.e., they simultaneously belong to the same free-energy basin. Therefore the key indicator of the ergodicity breaking process is $F(q)$. From Eqs. (31) and (32) it follows that the normalized quantity $\zeta_q = F(q)/G(q)$ is related to self-energy $\Sigma_F(q)$ through the nonperturbative relation:

$$\frac{\zeta_q}{1 - \zeta_q} = G(q)\Sigma_F(q). \quad (34)$$

Evaluation of Σ_F up to one-loop order [15] in terms of the cubic vertex $V(123)$ introduced in Eq. (14) obtains the integral equation for the so-called nonergodicity parameters $\{\zeta_q\}$ s. Using Eq. (28) for the matrix, Σ , the diagonal and off-diagonal parts are obtained in one-loop approximation as

$$\tilde{\Sigma}_G(q) = \sum_{\mathbf{k}} \tilde{V}_{\mathbf{q}-\mathbf{k},\mathbf{k}} G(k)G(|\mathbf{q} - \mathbf{k}|), \quad (35)$$

$$\tilde{\Sigma}_F(q) = \sum_{\mathbf{k}} \tilde{V}_{\mathbf{q}-\mathbf{k},\mathbf{k}} F(k)F(|\mathbf{q} - \mathbf{k}|). \quad (36)$$

The common vertex function at one-loop level is $\tilde{V}_{\mathbf{k},\mathbf{k}'}$

$$\tilde{V}_{\mathbf{k},\mathbf{k}'} = 2\rho_0[1 + \tilde{c}^{(3)}(\mathbf{k}, \mathbf{k}')^2 G(k)G(k')]. \quad (37)$$

Hence at the one-loop order, Eq. (34) obtains the following integral equation for the ζ_q s:

$$\frac{\zeta_q}{1 - \zeta_q} = G(q) \int \frac{d\mathbf{k}}{(2\pi)^3} V_{\mathbf{k},\mathbf{q}-\mathbf{k}} \zeta_k \zeta_{|\mathbf{q}-\mathbf{k}|}. \quad (38)$$

The vertex function $V_{\mathbf{k},\mathbf{k}'}$ is given above in Eq. (37).

The contribution to the cubic vertex $V_{\mathbf{k},\mathbf{k}'}$ from both \mathcal{H}_{id} and \mathcal{H}_{ex} of \mathcal{H} are important. At the Gaussian level, we keep terms up to quadratic order in density fluctuations for both \mathcal{H}_{id} and \mathcal{H}_{ex} and obtain the usual Ornstein-Zernike expression for the equal time density correlation,

$$S(k) = \frac{1}{1 - \rho_0 c^{(2)}(k)}. \quad (39)$$

Beyond the Gaussian field theory of quadratic fluctuations, the expansion of logarithmic term and three-point direct correlation $c^{(3)}$ contribute to terms involving cubic powers of the density fluctuations. For localized density profiles, this simple expansion of the functional \mathcal{H}_{id} in terms of $\delta\rho(\mathbf{x})$ works up to length scales of size of the sphere. For the interaction-part \mathcal{H}_{ex} , similar contributions involve higher-order direct correlation functions $c^{(n)}$, for $n \geq 3$, and these are small at large wave vectors by construction. We use a large wave vector cut off to keep the free-energy expansion in density fluctuations $\delta\rho$ valid in the present model. The NEP $F(q)$ represent the overlap of density fluctuations of different basins. Large wave vectors are assumed to signify the intrabasin dynamics or vibrational motion and are ignored. To consider the role of a wave vector cutoff needed in this model, we parametrize the inhomogeneous density $\rho(\mathbf{x})$ as

$$\rho(\mathbf{x}) = \sum_i \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \exp[-\alpha(\mathbf{x} - \mathbf{R}_i)^2], \quad (40)$$

in terms of Gaussian profiles centered around a random set of lattice points $\{\mathbf{R}_i\}$. The width of the density profiles described in Eq. (40) are $l \sim \alpha^{-1/2}$, and the mass is localized within lengths less than l . The ideal gas part of the free-energy functional is given in Eq. (9). For smaller values of α , i.e., overlapping Gaussians centered at different sites $\{\mathbf{R}_i\}$, we evaluate the ideal gas part $\mathcal{H}_{id}[\rho]$ numerically. This involves computation of the integral given in (9) in terms of a site-site correlation function for the random structure $\{\mathbf{R}_i\}$ [17]. Using Bernal's random structure [18] for the latter, the ideal free energy per particle $f_{id}(l)$ is evaluated. The result is shown in lower inset of Fig. 1 against the corresponding choice of the variable l for density function $\rho(\mathbf{x})$. For a system of hard spheres of diameter σ the free-energy density $f_{id}(l)$ is plotted with the corresponding l for $\rho(\mathbf{x})$. Up to a cutoff l_0 , the $f_{id}(l)$ is close to the free energy \bar{f}_{id} of a completely uniform state. l_0 is less than size of the hardcore of a fluid particle. For the interaction part, \mathcal{H}_{ex} , the large wave vector contributions are small by construction, since the higher-order $c^{(n)}$'s are small for large k . This point is further discussed below concerning Fig. 3.

The three-point function $c^{(3)}(\mathbf{k}, \mathbf{k}')$, in the right hand side of Eq. (38), is calculated as a convolution of a ternary function $t(r)$ following Ref. [19]. The calculation of the three-point

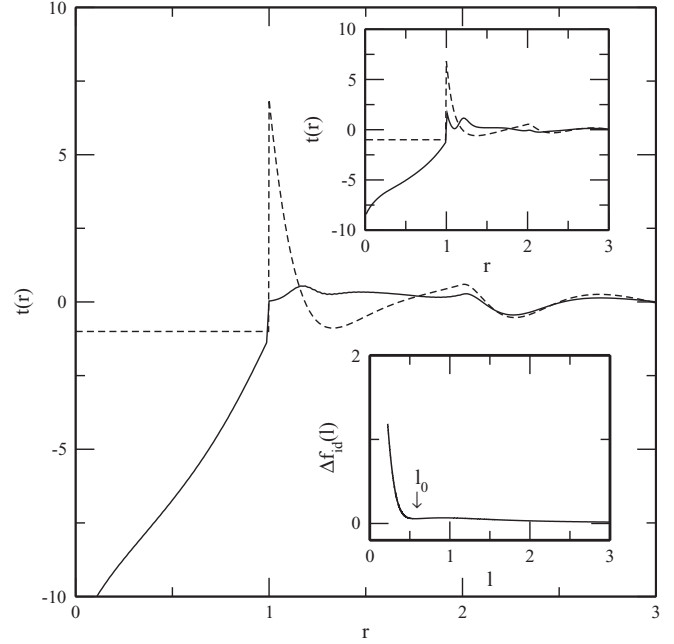


FIG. 1. Main panel (upper inset): The ternary function $t(r)$ as solid line and $h(r) = g(r) - 1$ as dashed line vs. r/σ for packing $\eta = .594 (.554)$ using the Percus-Yevick (Rodger-Young) input structure. Lower inset: $\Delta f_{id}(l)$ (see text) in units of β vs. l/σ with arrow at $l_0 \sim .60\sigma$ for wave number cutoff.

functions is described in Appendix B. For $t(r) \equiv g(r) - 1 = h(r)$, this method produces superposition approximation for $c^{(3)}(\mathbf{k}, \mathbf{k}')$. The plot of ternary function $t(r)$ vs. distance r in units of σ are shown in Fig. 1 for packing fraction $\eta = .594(.554)$ in the main panel (inset). The intrareplica correlation $G(q)$ is treated as an input here and is approximated in terms of structure factor obtained respectively using Percus-Yevick solutions [20] and Rogers-Young Bridge

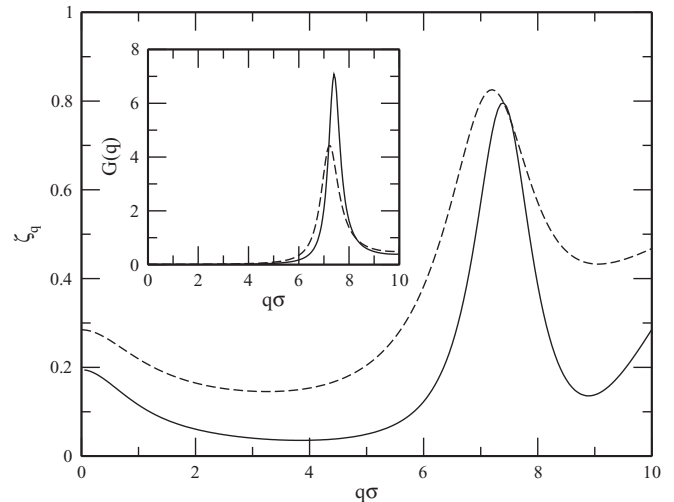


FIG. 2. The nonergodicity parameter ζ_q vs. $q\sigma$ at the transition point, $\eta_c = .594$ (solid) and $\eta_c = .554$ (dashed) respectively for input $G(q)$ from Percus-Yevick [20] and Rogers-Young [21]. The inset shows corresponding $G(q)$ s.

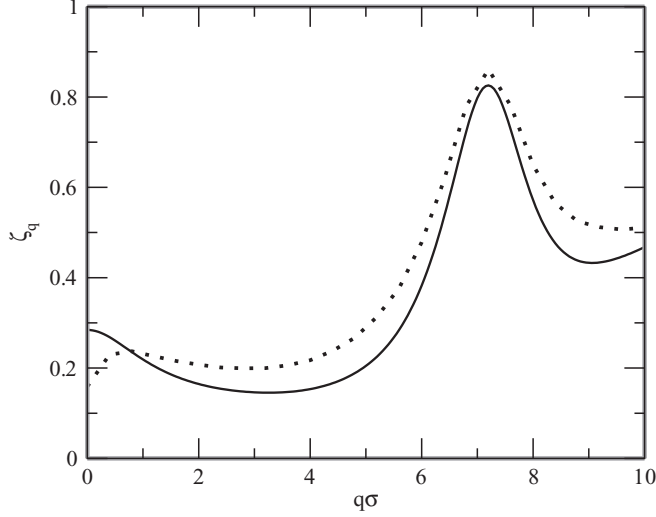


FIG. 3. The off-diagonal correlation $\zeta_q(q)$ vs. $q\sigma$ at packing $\eta_c = .554$ using the Roger-Young closure static structure factor as input. Solid line shows $\zeta_q(q)$ results corresponding to wave vector cutoff $q_{\max}\sigma = 10$. Dotted line is the same result with additional density fluctuations up to wave vector $k_{\max}\sigma = 20$ being included in \mathcal{H}_{ex} . The transition point in this case is lower at $\eta_c = .540$.

function method [21]. We also show in this figure the corresponding results for $h(r) = g(r) - 1$ in terms of the pair correlation function $g(r)$. For the superposition approximation $t(r)$ is identified with $h(r)$.

Self-consistent solutions for the ζ_q s are obtained from Eqs. (37) and (38) on a wave vector grid $.05/\sigma$ extending to a maximum of $2\pi/l_0$. At the transition, the NEPs $\{\zeta_q\}$ s over the wave vector grid become nonzero. At packing fractions, $\eta_c = .594$ and $.554$, respectively corresponding to Percus-Yevick and Rogers-Young structure factors, we obtain a nonzero set $\{\zeta_q\}$. See Fig. 2 for results for the NEPs ζ_q vs. $q\sigma$ while the inset shows the corresponding intrareplica correlations used as an input in the calculations. To consider the role of the wave vector cutoff on the NEP solutions in the interaction part \mathcal{H}_{ex} we consider also increasing the cutoff value to $20\sigma^{-1}$ from $10\sigma^{-1}$, and the result is shown in Fig. 3. At packing $\eta_c = .554$, we show the off-diagonal correlation ζ_q vs. $q\sigma$ for these two choices of the upper cutoff in the set of integral equations. The results for the NEP in the two cases are close, and the inclusion of shorter wavelength contributions for the interaction do produce drastic effects.

V. THE CONFIGURATIONAL ENTROPY

The configurational entropy S_c is calculated from the relation (7). For this, a nonperturbative expression for the free energy $\mathcal{F}(\beta, m)$ for the composite system of m identical replicas, defined in Eq. (5), is first obtained. To facilitate the calculation, a symmetric field U_{ab} ($U_{ab} = U_{ba}$) is included in the Gaussian part of the Hamiltonian $\mathcal{H}[\{\phi_a\}]$ in Eq. (5),

$$\mathcal{H}_0[\{\phi_a\}] = \frac{1}{2} \sum_{a,b} \phi_a \mathcal{G}_{0ab}^{-1} \phi_b + \frac{1}{2} \sum_{a,b} \phi_a U_{ab} \phi_b, \quad (41)$$

The full two-point function \mathcal{G}_{ab} is obtained by taking a derivative with respect to the current U_{ab} of the logarithm of partition

function \mathcal{W} which is defined in Eq. (5). Finally, the current U_{ab} is set equal to zero:

$$G_{ab} = - \frac{\delta}{\delta U_{ab}} \ln \mathcal{W} \Big|_{U=0}. \quad (42)$$

Due to the inclusion of the field U_{ab} the Dyson equation (27) is also modified to the following form:

$$\mathcal{G}_{ab}^{-1} = \{\mathcal{G}_0^{-1}\}_{ab} + U_{ab} - \Sigma_{ab}. \quad (43)$$

Hence variation of $\ln \mathcal{W}$ is obtained as in terms of \mathcal{G} and U ,

$$-\delta \ln \mathcal{W} = \text{Tr}\{\mathcal{G}\delta U\}. \quad (44)$$

The modified Dyson equation (43) is used to express δU in terms of $\delta\mathcal{G}^{-1}$ and $\delta\Sigma$. With this the right-hand side of Eq. (44) reduces to the form

$$-\delta \ln \mathcal{W} = \text{Tr}\{\mathcal{G}\delta\mathcal{G}^{-1}\} + \text{Tr}\{\mathcal{G}\delta\Sigma\} = \text{Tr}\{\mathcal{G}\delta\mathcal{G}^{-1}\} + \delta\text{Tr}\{\Sigma\mathcal{G}\} - \text{Tr}\{\Sigma[\delta\mathcal{G}]\}. \quad (45)$$

Next, we make use of the following identity, which holds for $m \times m$ square matrices

$$\text{Tr}\{\mathcal{G}\delta\mathcal{G}^{-1}\} = \delta[\text{Tr}\{\ln \mathcal{G}^{-1}\}], \quad (46)$$

where the variations are with respect to the elements of the matrix \mathcal{G}_{ij} for fixed U and m . The corresponding derivative of $\text{Tr} \ln \mathcal{G}^{-1}$ with respect to \mathcal{G}_{ab} is obtained as

$$\frac{\delta}{\delta \mathcal{G}_{ab}(q)} \text{Tr}\{\ln \mathcal{G}^{-1}\} = \sum_{\mathbf{k}} \mathcal{G}_{ij}(\mathbf{k}) \frac{\delta \mathcal{G}_{ij}^{-1}(\mathbf{k})}{\delta \mathcal{G}_{ab}(q)}. \quad (47)$$

We replace the functional derivative of \mathcal{G}_{ij}^{-1} with that of the self-energy Σ_{ij} by using Eq. (43). Next, we confine the further analysis to the one-loop expression (28) for the self-energy matrix Σ_{ab} , which arises from the cubic vertices V in the free energy \mathcal{H} . After some simple algebra involving functional derivatives, it follows that Eq. (47) simplifies to

$$\frac{\delta}{\delta \mathcal{G}_{ab}(q)} [\text{Tr}\{\ln \mathcal{G}^{-1}\}] = -2\Sigma_{ab}(q). \quad (48)$$

Using Eqs. (46) and (48) the free energy \mathcal{F} defined in Eq. (5) is obtained as

$$\mathcal{F}(m) = - \frac{1}{\beta m} \ln \mathcal{W} = \frac{1}{\beta m} \left[\frac{3}{2} \text{Tr}\{\ln \mathcal{G}^{-1}\} + \text{Tr}\{\Sigma\mathcal{G}\} - C_0(m) \right], \quad (49)$$

where $C_0(m)$ is an additive-constant independent of \mathcal{G}_{ij} . Using the above result for free energy $\mathcal{F}(m)$, the configurational entropy S_c is obtained from Eq. (7). In order to further simplify the form, we note from the respective expressions (19) and (29) for the $m \times m$ square matrices \mathcal{G} and Σ that both have the common form \mathcal{A} ,

$$\mathcal{A} = a_1 \mathbf{I} + a_2 \mathbf{E}, \quad (50)$$

where \mathbf{I} and \mathbf{E} are both $m \times m$ square matrices as defined with Eq. (19). We now make use of the following identity that holds [14,22] for a $m \times m$ square matrix \mathcal{A} which has the special form (50),

$$\frac{\partial}{\partial m} \left[\frac{1}{m} \text{Tr}\{\ln \mathcal{A}\} \right]_{m=1} = \left[\frac{a_2}{a_1 + a_2} \right] + \ln \left[1 - \frac{a_2}{a_1 + a_2} \right], \quad (51)$$

assuming that a_1 and a_2 are independent of m . Identifying \mathcal{A} with \mathcal{G}^{-1} , we obtain from (51)

$$\begin{aligned} & \frac{\partial}{\partial m} \left[\frac{1}{m} \text{Tr} \{ \ln \mathcal{G}^{-1} \} \right]_{m=1} \\ &= \sum_{\mathbf{k}} \left\{ \Sigma_F(\mathbf{k}) G(\mathbf{k}) + \ln [1 + \Sigma_F(\mathbf{k}) G(\mathbf{k})] \right\}. \end{aligned} \quad (52)$$

The product ΣG has also a form similar to (50) and trace of this matrix is obtained as

$$\text{Tr} \{ \Sigma \mathcal{G} \} = \sum_{\mathbf{k}} [m \Sigma_G(\mathbf{k}) G(\mathbf{k}) + m(m-1) \Sigma_F(\mathbf{k}) F(\mathbf{k})]. \quad (53)$$

Hence using Eqs. (7), (49), and (52), the configurational entropy \mathcal{S}_c is obtained as

$$\begin{aligned} \mathcal{S}_c &= \frac{1}{2} \sum_{\mathbf{k}} \{ 3 \ln [1 + G(\mathbf{k}) \Sigma_F(\mathbf{k})] \\ &\quad - [3G(\mathbf{k}) - 2F(\mathbf{k})] \Sigma_F(\mathbf{k}) \} + \mathcal{S}_0. \end{aligned} \quad (54)$$

The quantity $\mathcal{S}_0 = d/dm [\mathcal{C}_0(m)/m]_{m=1}$ is independent of density and treated as a the parameter in the model to obtain the Kauzmann point. Writing the self-energy Σ_F Eq. (54) in terms of the one-loop approximation $\tilde{\Sigma}_F$ using Eq. (36), the configurational entropy \mathcal{S}_c is obtained in terms of the nonergodicity parameters $\{\zeta_{\mathbf{k}}\}$,

$$\mathcal{S}_c = \sum_{\mathbf{k}} \left[\frac{3}{2} \ln \left(\frac{1}{1 - \zeta_{\mathbf{k}}} \right) - \frac{\zeta_{\mathbf{k}}}{1 - \zeta_{\mathbf{k}}} \left(\frac{3}{2} - \zeta_{\mathbf{k}} \right) \right] + \mathcal{S}_0. \quad (55)$$

Using the density dependence of \mathcal{S}_c , we analyze the corresponding dependence of the derivative, and doing a power-law fit of the divergence of the derivative $-d\mathcal{S}_c/d\eta$ to the form $A(\eta_K - \eta)^{\nu'}$, we estimate the Kauzmann point η_K . We show this in the inset of Fig. 4. After η_K , and ν' are known, we fit \mathcal{S}_c to the form $A_1(\eta_K - \eta)^\nu$, ($A_1 = A/\nu$, and $\nu = \nu' + 1$) treating \mathcal{S}_0 as a density-independent constant. The value of \mathcal{S}_0 is fixed by the choice that the configurational entropy is zero at the Kauzmann point η_K . With an increase of density, the NEPs $\{\zeta_{\mathbf{k}}\}$ increases, and hence the first term in the right-hand side of the expression (55) also increases in magnitude. The configurational entropy \mathcal{S}_c decreases with the increase of density as \mathcal{S}_0 is chosen to be positive. The constant \mathcal{S}_0 in the present context signifies the large number of minima appearing close to freezing point. We obtain the Kauzmann points $\eta_K = .620$, and $.605$ for the two respective inputs of intrareplica correlation from Percus-Yevick and Rogers-Young methods. These η_K values are comparable to results from other studies [9,11,23].

VI. DYNAMIC-CORRELATIONS AND REPLICA-CORRELATIONS

The MCT [24] of dense liquids presents the scenario of a transition from an ergodic to a nonergodic state and is relevant in the present context. This ergodicity-nonergodicity transition of MCT is driven by a dynamic feedback mechanism [25]. The model is derived in terms of hydrodynamic modes' couplings and follows from the equations of fluctuating nonlinear hydrodynamics (FNH). These equations represent

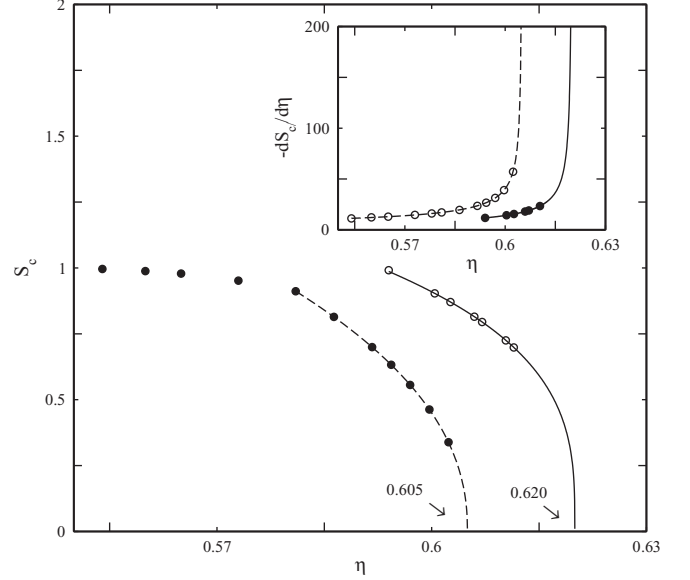


FIG. 4. Configurational entropy \mathcal{S}_c scaled with its value at the transition point (see text) vs. packing fraction η , for structure factors from Percus-Yevick (open circles) and Rogers-Young (closed circles). Solid (dashed) line is power-law fit extrapolating to zero at corresponding $\eta = \eta_K$. Inset: $-d\mathcal{S}_c/d\eta$ vs. η , respective symbols same as in the main panel. Solid (dashed) line shows power-law divergence at η_K .

microscopic conservation laws for a many-particle system [26]. The corresponding order parameter for the dynamic transition of MCT is the long-time limit of the correlation of density fluctuations $\mathcal{C}(q, t \rightarrow \infty) = f_q$. The density fluctuations are defined around the uniform state corresponding to the global minimum of the free energy. The NEPs depicted in earlier sections of the present paper and are different from the $\{f_q\}$ s corresponding to the dynamic transition of MCT. However, in both cases, the coupled set of integral Eqs. (38) are the same, except for a difference between the respective vertices $V_{\mathbf{k},\mathbf{k}'}$. The vertex in MCT is a consequence of non-linear driving term $\rho \nabla_i (\delta \mathcal{H} / \delta \rho)$ in the FNH equation [27] for the momentum density. The corresponding quadratic coupling of density fluctuations comes from the interaction part \mathcal{H}_{ex} and involves the two-point function $\tilde{c}^{(2)}$,

$$V_{\mathbf{k},\mathbf{k}'} = \rho_0 \{ (\hat{q} \cdot \mathbf{k}) \tilde{c}(k') + (\hat{q} \cdot \mathbf{k}') \tilde{c}(k) \}^2 G(k) G(k'). \quad (56)$$

Additional corrections involving $\tilde{c}^{(3)}$ occur [28] from the cubic order term in (10). However, the primary part of the mode-coupling integral comes from the Gaussian free energy, and hence the feedback mechanism of MCT is of dynamic origin. In this regard, it is helpful to note that, unlike the case of a replica model, the logarithmic term in the ideal gas part \mathcal{H}_{id} generates a linear term $\nabla_i \rho$ for the dynamics in MCT.

In contrast, the nonzero inter-replica correlations $\{\zeta_{\mathbf{q}}\}$ in Eq. (38) arise from the *non*-Gaussian part of the density-functional Hamiltonian (10), and the corresponding vertex function (37) involves $\tilde{c}^{(3)}(\mathbf{k}, \mathbf{k}')$, signifying the role of multiparticle correlations besides entropic contributions. In some works, however, the two approaches mentioned above are linked by treating the MCT with modification of the

structural inputs obtained from replica models. Furthermore, the MCT memory kernels (56) have been obtained [29–31] in some works by simply invoking the replica formulation [32] on the static correlations of the metastable liquid at the two-point level. Corrections to these models with the so-called replicated hyper-netted-chain approximation indicated the importance of static three-particle correlations [33] in theory. However, similarities in the integral equations (38) for the respective order parameters for the dynamic transition of MCT and the spontaneous ergodicity breaking transition with a replica approach (considered in the present work) goes beyond and occurs without the structure functions being modified.

In MCT, the increased cooperativity in the particle movements in a dense liquid are accounted through the coupling of density fluctuations. From this perspective, the theory is essentially a correction to Boltzmann-Enskog models (mean-field) of transport based on uncorrelated collisions. On the other hand, keeping analogy with spin-glass [32] models, MCT itself has often been considered as a mean-field description and becomes exact [34,35] for spatial dimension $d \rightarrow \infty$ in which all higher-order correlations are ignored. In this limit, a sharp dynamical glass transition associated with perfect caging, and a power-law divergence of viscosity is predicted [36,37]. For finite dimensions, there are corrections over the mean-field model, which smooths the dynamical glass transition, though a strong remnant of the latter remains. The full set of nonlinearities present in the FNH equations for a compressible liquid ensured, through fluctuation-dissipation constraints, that the NEP's of the ideal transition goes to zero. Hopping between localized cages formed by neighboring particles in the nonergodic state was also considered [38] to analyze the absence of the dynamic transition MCT for finite dimensions. While the dynamic transition of MCT is absent for finite dimensions, an entropy crisis sets in with further supercooling or density increase. The present work using replicas, and with the assumption of fragmentation of the FEL, provides a model for this sharp decrease of configurational entropy S_c and calculation of the Kauzmann point. In both MCT and the present work, the respective results are limited to the one-loop level.

VII. DISCUSSION

We present a statistical mechanics model for an atomic system deep in the metastable region, beyond the range where conventional mode-coupling theory applies. The theoretical formulation is based on a scenario following the works of Kirkpatrick-Thirumalai and R. Monasson. We study a field-theoretic model for the many-particle system using the classical DFT. The corresponding partition function is calculated using the scenario of fragmentation of the FEL in terms of basins of local minima and through a mapping to a composite system of m identical replicas. The configurational entropy is estimated in terms of the number of such minima. The corresponding nonergodicity parameter is defined as the overlap correlations of density fluctuations in two identical replicas. Here we take into account the nonlocal structural dependence, going beyond a Landau-type expansion [14,39,40] for the effective Hamiltonian in a functional form which includes including effects of multiparticle correlations. The

present model's key contribution to the inter-replica coupling is rooted in the non-Gaussian contribution to free energy. It is symbolized in simplest terms with the cubic vertex $V(123)$ in Eq. (14). The NEP ζ_q is zero if the Σ_F (a contribution coming from the non-Gaussian parts) is zero, as can be seen from Eq. (34). Thus the NEP or the inter-replica coupling is directly linked with the vertex V .

The present calculation provides an understanding of the configurational entropy crisis based on the structural information. In this respect, it is useful to note that a microscopic-level description that explains how the dynamics cross over from a continuum fluid-type motion to the formation of a barrier (to transport) with the spontaneous fragmentation of the free-energy landscape into distinct basins is desirable but has not yet been formulated. Our work is a step in this direction using the structure as the only input. Based on the assumption on the FEL outlined above, the present work shows how the entropy crisis can be understood using the same *nonlocal* free-energy functional, as used in obtaining the MCT, and thus constitutes a valuable step. With the fragmented FEL, as the free-energy basins get deep, the nonergodic behavior sets in and is signalled through nonzero overlap F between density fluctuations in identical replicas. The fall of configurational entropy S_c approaching the Kauzmann point η_K is obtained in a first-principles calculation here including effects of multiparticle correlations. This result is a qualitative improvement over MCT in the closer vicinity of an approaching glass transition.

ACKNOWLEDGMENTS

P.V. acknowledges UGC, India, and S.P.D. acknowledges the JC Bose fellowship Project Science and Engineering Board (SERB), Department of Science and Technology, Govt. of India for financial support.

APPENDIX A: DYSON EQUATION AND SELF-ENERGY

In this Appendix, we analyze Eq. (22) to obtain the so-called Dyson equation (27), which defines the inverse of the correlation function matrix \mathcal{G} in terms of the self-energy matrix Σ . From the analysis the self-energy Σ is obtained in a closed form (26) in terms of full correlation functions $\{G\}$. We do this in the two following steps.

First, we note that using the identity (24) the last term on the left-hand side of Eq. (22) is obtained in the form,

$$\begin{aligned} V^{abc}(\bar{1}\bar{2}\bar{3})\mathcal{G}_{\bar{b}\bar{a}}(\bar{2}\bar{4}) \left[-\frac{\delta\mathcal{G}_{\bar{d}\bar{e}}^{-1}(\bar{4}\bar{5})}{\delta\mu^b(2)} \right] \mathcal{G}_{\bar{e}\bar{c}}(\bar{5}\bar{3}) \\ = V^{abc}(\bar{1}\bar{2}\bar{3})\mathcal{G}_{\bar{b}\bar{a}}(\bar{2}\bar{4})\mathcal{P}^{\bar{d}\bar{e}b}(\bar{4}\bar{5}\bar{2})\mathcal{G}_{\bar{e}\bar{c}}(\bar{5}\bar{3}). \end{aligned} \quad (\text{A1})$$

The quantity within square bracket is denoted as the vertex function $\mathcal{P}^{\bar{d}\bar{e}b}(\bar{4}\bar{5}\bar{2})$. In the expression (A1) and rest of this Appendix we adopt, as in the main text, the following notations: The barred indices like $\{\bar{1}, \bar{2}, \dots\}$ are considered respectively in combination with the roman symbols $\{a, b, \dots\}$, etc. The numbers $\{1, 2, \dots\}$ indicate the spatial coordinates, while the roman letters $\{a, b, \dots\}$ stand for the replica indices. We also apply the summation convention that repeated indices are summed over or integrated out.

Next, we obtain an equation for the vertex \mathcal{P} . From Eq. (21), we express the currents $\{\mu^a(1)\}$ in terms of $\{G(1), G(12)\}$ order by order in a perturbation theory. We, therefore, make a change of variables from $\mu(1)$ to $\{G(1), G(12)\}$ and use the chain rule to write

$$\frac{\delta \mathcal{G}_{ab}^{-1}(12)}{\delta \mu^c(3)} = \frac{\delta \mathcal{G}_{ab}^{-1}(12)}{\delta \mathcal{G}_{\bar{c}}(\bar{3})} \frac{\delta \mathcal{G}_{\bar{c}}(\bar{3})}{\delta \mu^c(3)} + \frac{\delta \mathcal{G}_{ab}^{-1}(12)}{\delta \mathcal{G}_{\bar{c}\bar{d}}(\bar{3}\bar{4})} \frac{\delta \mathcal{G}_{\bar{c}\bar{d}}(\bar{3}\bar{4})}{\delta \mu^c(3)}. \quad (\text{A2})$$

Now substituting the functional identity (24) in the second term on the right-hand side of the relation (A2) we obtain

$$\frac{\delta \mathcal{G}_{ab}^{-1}(12)}{\delta \mu^c(3)} = \frac{\delta \mathcal{G}_{ab}^{-1}(12)}{\delta \mathcal{G}_{\bar{c}}(\bar{3})} \mathcal{G}_{\bar{c}\bar{c}}(\bar{3}\bar{3}) - \frac{\delta \mathcal{G}_{ab}^{-1}(12)}{\delta \mathcal{G}_{\bar{c}\bar{d}}(\bar{3}\bar{4})} \mathcal{G}_{\bar{c}\bar{e}}(\bar{3}\bar{5}) \frac{\delta \mathcal{G}_{\bar{e}\bar{f}}^{-1}(\bar{5}\bar{6})}{\delta \mu^c(3)} \mathcal{G}_{\bar{f}\bar{d}}(\bar{6}\bar{4}). \quad (\text{A3})$$

We use the Dyson equation (27) to replace the functional derivatives

$$\mathcal{P}^{abc}(123) = -\frac{\delta \mathcal{G}_{ab}^{-1}(12)}{\delta \mu^c(3)} \longrightarrow \frac{\delta \Sigma_{ab}(12)}{\delta \mu^c(3)} \quad (\text{A4})$$

and obtain Eq. (A3) in the form

$$\frac{\delta \Sigma_{ab}(12)}{\delta \mu^c(3)} = \frac{\delta \Sigma_{ab}(12)}{\delta \mathcal{G}_{\bar{c}}(\bar{3})} \mathcal{G}_{\bar{c}\bar{c}}(\bar{3}\bar{3}) + \frac{\delta \Sigma_{ab}(12)}{\delta \mathcal{G}_{\bar{c}\bar{d}}(\bar{3}\bar{4})} \mathcal{G}_{\bar{c}\bar{e}}(\bar{3}\bar{5}) \frac{\delta \Sigma_{\bar{e}\bar{f}}(\bar{5}\bar{6})}{\delta \mu^c(3)} \mathcal{G}_{\bar{f}\bar{d}}(\bar{6}\bar{4}). \quad (\text{A5})$$

In terms of the three-point vertex function $\mathcal{P}^{abc}(123)$, Eq. (A5) is written as the following self-consistent relation:

$$\mathcal{P}^{abc}(123) = \Gamma^{abc}(12\bar{3}) \mathcal{G}_{\bar{c}\bar{c}}(\bar{3}\bar{3}) + U^{abc\bar{d}}(12\bar{3}\bar{4}) \mathcal{G}_{\bar{c}\bar{e}}(\bar{3}\bar{5}) \mathcal{G}_{\bar{d}\bar{f}}(\bar{4}\bar{6}) \mathcal{P}^{\bar{e}\bar{f}c}(\bar{5}\bar{6}\bar{3}), \quad (\text{A6})$$

where the three- and four-point vertex functions $\Gamma^{abc}(123)$ and $U^{abcd}(1234)$ are respectively defined as

$$\Gamma^{abc}(123) \equiv \frac{\delta \Sigma(12)}{\delta \mathcal{G}_c(3)}, \quad (\text{A7})$$

$$U^{abcd}(1234) \equiv \frac{\delta \Sigma_{ab}(12)}{\delta \mathcal{G}_{cd}(34)}. \quad (\text{A8})$$

We now substitute the expression (A6) for \mathcal{P} in the expression (A1) to obtain a closed relation for the self-energy matrix Σ . We are interested in one-loop corrections and are including here only up to third-order vertex (involving three-point direct correlation functions $c^{(3)}$ in the DFT Hamiltonian). It is sufficient to keep only the first term on the right-hand side of Eq. (A6). Making this substitution in the expression (A1), and using the same in the last term on the left-hand side of the Eq. (22), we obtain

$$\begin{aligned} & \left\{ \mathcal{G}_0^{-1} \right\}_{ab}(\bar{1}\bar{2}) \mathcal{G}_{bb}(\bar{2}\bar{2}) + 2V^{abc}(1\bar{2}\bar{3}) [\mathcal{G}_{bb}(\bar{2}\bar{2}) \mathcal{G}_{\bar{c}}(\bar{3}) \\ & + \mathcal{G}_{\bar{b}}(\bar{2}) \mathcal{G}_{\bar{c}\bar{b}}(\bar{3}\bar{2}) + \mathcal{G}_{\bar{b}\bar{d}}(\bar{2}\bar{4}) \frac{\delta \Sigma_{\bar{d}\bar{e}}(\bar{4}\bar{5})}{\delta \mathcal{G}_{\bar{f}}(\bar{6})} \mathcal{G}_{\bar{e}\bar{c}}(\bar{5}\bar{3}) \mathcal{G}_{\bar{f}\bar{b}}(\bar{6}\bar{2})] \\ & = \delta(12) \delta_{ab}. \end{aligned} \quad (\text{A9})$$

We use the symmetry of the bare cubic vertex V for its indices and interchange the dummy index sets $\{\bar{2}, \bar{b}\} \leftrightarrow \{\bar{6}, \bar{f}\}$ in the last term on the left-hand side of Eq. (A9) to write the latter equation in the form:

$$\left[\left\{ \mathcal{G}_0^{-1} \right\}_{ab}(\bar{1}\bar{2}) - \Sigma_{ab}(\bar{1}\bar{2}) \right] \mathcal{G}_{bb}(\bar{2}\bar{2}) = \delta(12) \delta_{ab}, \quad (\text{A10})$$

where the matrix Σ is obtained as

$$\begin{aligned} \Sigma_{ab}(12) &= -2V^{abc}(1\bar{2}\bar{3}) \mathcal{G}_{\bar{c}}(\bar{3}) - V^{abc}(1\bar{2}\bar{3}) \mathcal{G}_{\bar{b}\bar{d}}(\bar{2}\bar{4}) \\ &\times \left[\frac{\delta \Sigma_{\bar{d}\bar{e}}(\bar{4}\bar{5})}{\delta \mathcal{G}_{\bar{b}}(\bar{2})} \mathcal{G}_{\bar{e}\bar{c}}(\bar{5}\bar{3}) \right]. \end{aligned} \quad (\text{A11})$$

We use the derivative in the second term on the right-hand side of Eq. (A12) to lowest order in the bare vertex V and obtain the following expression Σ to leading orders:

$$\begin{aligned} \Sigma_{ab}(12) &= -2V^{abc}(1\bar{2}\bar{3}) \mathcal{G}_{\bar{c}}(\bar{3}) \\ &+ 2V^{abc}(1\bar{2}\bar{3}) \mathcal{G}_{\bar{b}\bar{d}}(\bar{2}\bar{4}) \mathcal{G}_{\bar{c}\bar{e}}(\bar{3}\bar{5}) V^{\bar{d}\bar{e}b}(\bar{4}\bar{5}\bar{2}). \end{aligned} \quad (\text{A12})$$

APPENDIX B: THREE-POINT DIRECT-CORRELATION FUNCTION

A key aspect of the present model is calculating the effects of multiparticle correlations on configurational entropy of the deeply metastable state. Cooperative effects in a many-particle system is generally expressed through corresponding functions $g^{(s)}(\mathbf{r}_1, \dots, \mathbf{r}_s)$, defined in terms of the corresponding reduced distribution function,

$$\rho^{(s)}(\mathbf{r}_1, \dots, \mathbf{r}_s) = \rho_0^s g^{(s)}(\mathbf{r}_1, \dots, \mathbf{r}_s). \quad (\text{B1})$$

We focus here on the first two functions, $g^{(2)}(\mathbf{r})$ and $g^{(3)}(\mathbf{r}, \mathbf{r}')$, respectively, at the two and three particle levels. The corresponding Fourier transforms are related to respective equilibrium ensemble averages of products of microscopic densities $\rho(\mathbf{r}_i)$ over the positions of the particles $\{\mathbf{r}_i\}$ for $i = 1, \dots, N$ and are denoted as $G(\mathbf{k})$ and $G(\mathbf{k}, \mathbf{k}')$,

$$G^{(2)}(\mathbf{k}) = N^{-1} \langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle, \quad (\text{B2})$$

$$G^{(3)}(\mathbf{k}, \mathbf{k}') = N^{-1} \langle \rho_{\mathbf{k}} \rho_{\mathbf{k}'} \rho_{-\mathbf{k}-\mathbf{k}'} \rangle, \quad (\text{B3})$$

where $\rho_{\mathbf{k}}$ denotes the Fourier transform of the microscopic density,

$$\rho_{\mathbf{k}} = \sum_{\alpha=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_{\alpha}). \quad (\text{B4})$$

Generally, the higher-order correlation functions are approximated in terms of lower-order correlations. A typical approximation for the three-point correlation is the so-called superposition approximation or the Kirkwood approximation, which relates $g^{(3)}$ to $g^{(2)}$ as

$$g^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = g^{(2)}(\mathbf{r}' - \mathbf{r}'') g^{(2)}(\mathbf{r} - \mathbf{r}') g^{(2)}(\mathbf{r} - \mathbf{r}''). \quad (\text{B5})$$

Now, assuming translational invariance, this is independent of the choice of origin and hence choosing that at \mathbf{r}'' , we obtain,

$$g^{(3)}(\mathbf{r}, \mathbf{r}') = g^{(2)}(\mathbf{r}) g^{(2)}(\mathbf{r}') g^{(2)}(\mathbf{r} - \mathbf{r}'). \quad (\text{B6})$$

Further, in an isotropic system for the two-point function, we take $g(\mathbf{r})$ to be a function of r only. At the next level, a similar closure in the Fourier space is the convolution approximation

in which $G^{(3)}(\mathbf{k}, \mathbf{k}')$ is expressed in terms of the two-point quantities, $G^{(2)}(\mathbf{k})$ s,

$$G^{(3)}(\mathbf{k}, \mathbf{k}') = G^{(2)}(\mathbf{k})G^{(2)}(\mathbf{k}')G^{(2)}(|\mathbf{k} + \mathbf{k}'|). \quad (\text{B7})$$

1. Direct correlation functions

For expressing the interaction part of the effective Hamiltonian the so-called direct correlation functions $c^{(i)}(\mathbf{r}_1 \dots \mathbf{r}_i)$, for $i = 2, 3, \dots$ are of particular relevance. Effects of multiparticle correlations are included in the present theoretical model through the inclusion of the non-Gaussian terms with corresponding vertices in the density-functional expression (12) for the effective Hamiltonian [41,42]. The Gaussian model is renormalized with the self-energy matrix Σ , defined in the Dyson equation. The effects from the non-Gaussian parts in the effective Hamiltonian are included in Σ and calculated perturbatively as correlation functions' convolutions. The self-energy contributions also include vertex functions involving the $c^{(i)}$ s of cubic and higher orders. At the simplest level, our primary focus is on the three-point level involving $c^{(3)}(\mathbf{r}, \mathbf{r}')$ for a translational invariant system. Increment of the two-point function $c^{(2)}(\mathbf{r})$ corresponding to the change of the density function $\rho(\mathbf{r}) + \Delta\rho(\mathbf{r})$ to $\rho(\mathbf{r})$ is obtained in terms of the three-point function $c^{(3)}$ with following integral relation:

$$\begin{aligned} c^{(2)}[\mathbf{r}; \rho + \Delta\rho] - c^{(2)}[\mathbf{r}; \rho] &= \int d\mathbf{r}' \left[\frac{\delta c^{(2)}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \right] \Delta\rho(\mathbf{r}') \\ &= \int d\mathbf{r}' c^{(3)}[\mathbf{r}, \mathbf{r}'; \rho] \Delta\rho(\mathbf{r}'). \end{aligned} \quad (\text{B8})$$

For a homogeneous system, the density $\rho(\mathbf{r}) = \rho_0$ and $\Delta\rho(\mathbf{r}) = \Delta\rho_0$ on the right-hand side of (B8) can be taken out of the integral reducing the above relation to a simple expression for the partial derivative of the two-point function $c^{(2)}(\mathbf{r}; \rho_0)$,

$$\frac{\partial c^{(2)}(r, \rho_0)}{\partial \rho_0} = \int c^{(3)}(\mathbf{r}, \mathbf{r}'; \rho_0) d\mathbf{r}'. \quad (\text{B9})$$

The direct-correlation functions $c^{(i)}$ are linked to corresponding multiparticle correlation functions $g^{(i)}$ or equivalently to $G^{(i)}$ through the so-called Ornstein-Zernike relations. At the two-point level, the direct correlation function $c^{(2)}$ for the liquid is related to the corresponding structure function $G^{(2)}$ through the Ornstein-Zernike relation. The Fourier transform $\tilde{c}^{(2)}(k)$ of $c^{(2)}(r)$ is related to $G^{(2)}(k)$ as

$$G^{(2)}(k) = \frac{1}{1 - \tilde{c}^{(2)}(k)}. \quad (\text{B10})$$

$$\tilde{c}^{(3)}(\mathbf{k}, \mathbf{k}') = \int \frac{dq}{(2\pi)^2} q^2 t(q) \sum_{l, l'} \left\{ \int d(\cos\theta) f_l(k, q) f_{l'}(k', q) P_l[\cos(\theta)] P_{l'}[\cos(\theta')] \right\}, \quad (\text{B17})$$

where θ' denote the angle $\{\mathbf{k}', -\mathbf{q}\}$. Integration for the vector \mathbf{q} is written here in polar coordinates having θ as the polar angle and with assumption of azimuthal symmetry. The azimuthal symmetry is used so that $\phi = \phi'$, respectively the angles corresponding to θ and θ' . We denote $\gamma = \theta' - \theta$, and hence $\cos\theta' = \cos(\gamma)\cos(\theta) - \sin(\gamma)\sin(\theta)$. To calcu-

A factor of density ρ_0 is absorbed in $\tilde{c}(k)$ to make it dimensionless. At the three-point level, such relations have been generalized [43] in the form:

$$\begin{aligned} G^{(3)}(\mathbf{k}, \mathbf{k}') &= G^{(2)}(\mathbf{k})G^{(2)}(\mathbf{k}')G^{(2)}(|\mathbf{k} + \mathbf{k}'|) \\ &\times [1 + n_0^2 c^{(3)}(\mathbf{k}, \mathbf{k}')]. \end{aligned} \quad (\text{B11})$$

Comparing (B7) and (B11), it follows that the convolution approximation (B7) amounts to assuming $c^{(3)}(\mathbf{k}, \mathbf{k}') = 0$. The next step in our analysis is estimating $c^{(3)}(\mathbf{r}, \mathbf{r}')$, with an expression like that of the Kirkwood approximation (B6), in terms of a function $t(r)$:

$$c^{(3)}(\mathbf{r}, \mathbf{r}') = t(\mathbf{r})t(\mathbf{r}')t(\mathbf{r} - \mathbf{r}'). \quad (\text{B12})$$

For the choice $t(r)(r) - 1 = h(r)$, this method [19] produces superposition approximation for $c^{(3)}(\mathbf{k}, \mathbf{k}')$. Fourier transform of the triplet correlation function $c^{(3)}(\mathbf{r}, \mathbf{r}')$ in k space is

$$c^{(3)}(\mathbf{k}, \mathbf{k}') = \rho_0^2 \int d\mathbf{r} \int d\mathbf{r}' c^{(3)}(\mathbf{r}, \mathbf{r}') \exp(i\mathbf{k} \cdot \mathbf{r} + i\mathbf{k}' \cdot \mathbf{r}'). \quad (\text{B13})$$

Using the ansatz (B12) in definition (B13), the Fourier transform $c^{(3)}(\mathbf{k}, \mathbf{k}')$ is obtained after scaling with the factor ρ_0^2 as

$$\tilde{c}^{(3)}(\mathbf{k}, \mathbf{k}') = \int \frac{d\mathbf{q}}{(2\pi)^3} \hat{t}(\mathbf{q}) \hat{t}(\mathbf{k} + \mathbf{q}) \hat{t}(\mathbf{k}' - \mathbf{q}). \quad (\text{B14})$$

For an isotropic system $t(\mathbf{r})$ is a function of r only. If we choose $t(r)$ as $h(r) = g^{(2)}(r) - 1$, then $c^{(3)}(\mathbf{r}, \mathbf{r}')$ only contributes when all three particles are close. The Fourier transform $\hat{t}(\mathbf{k} + \mathbf{q})$ is also a function of $|\mathbf{k} + \mathbf{q}|$ only. Legendre polynomial expansion $\hat{t}(|\mathbf{k} + \mathbf{q}|)$ obtain

$$\hat{t}(|\mathbf{k} + \mathbf{q}|) = \sum_l f_l(k, q) P_l[\cos(\theta)], \quad (\text{B15})$$

where θ denotes the angle between $\{\mathbf{k}, \mathbf{q}\}$. Using the orthogonality property of Legendre polynomials, the coefficients $f_l(k, q)$ are obtained as

$$f_l(k, q) = \left(l + \frac{1}{2} \right) \int_{-1}^1 \hat{t}(|\mathbf{k} + \mathbf{q}|) P_l(\cos\theta) d(\cos\theta). \quad (\text{B16})$$

We now simplify the expression for $\tilde{c}^{(3)}(\mathbf{k}, \mathbf{k}')$ in the right-hand side of (B14) by using expansion in terms of Legendre polynomials [19,44]. Substituting the expansion Eq. (B15) of \hat{t} into Eq. (B14) we obtain

late the integral on right-hand side of Eq. (B17) we use the following expansion for $P_l(\cos\theta')$ in terms of the spherical harmonics involving θ and ϕ :

$$P_{l'}(\cos\theta') = \sum_{m=-l'}^{l'} b_{l'm} Y_{lm}(\theta, \phi). \quad (\text{B18})$$

For $\theta = 0$, $\cos \theta = 1$, and the corresponding Legendre polynomials $P_l^m(1) = 1$ for $m = 0$ and is equal to zero for all other values of m . On the other hand, $\cos \theta'$ is simply $\cos \gamma$. Hence taking $\theta = 0$ we obtain from Eq. (B18) the result $P_l(\cos \gamma) = b_{l0}$. Now multiplying Eq. (B18) with $P_l(\cos \theta)$ and integrating over $\cos \theta$ we obtain

$$\begin{aligned} & \int d(\cos \theta) P_l(\cos \theta) P_l(\cos \theta') \\ &= \frac{2}{2l+1} \delta_{ll'} b_{l0} = \frac{2}{2l+1} \delta_{ll'} P_l(\cos \gamma). \end{aligned} \quad (\text{B19})$$

So the formula (B17) reduces to the form

$$\tilde{c}^{(3)}(\mathbf{k}, \mathbf{k}') = \sum_l \mathcal{I}_l(k, k') P_l(\cos \gamma), \quad (\text{B20})$$

where the integral $\mathcal{I}_l(k, k')$ is obtained in terms of $f_l(k, q)$ defined in Eq. (B16) in the following form:

$$\mathcal{I}_l(k, k') = \frac{4\pi}{2l+1} \int q^2 t(q) f_l(k, q) f_l(k', q) \frac{dq}{(2\pi)^3}. \quad (\text{B21})$$

2. Numerical evaluation of $t(\mathbf{r})$

The function $t(r)$ is calculated using a Legendre polynomial expansion and solving the identity relation (B9) for the uniform state of density ρ_0 , with an iterative method. The value of function $t(r)$ is obtained by minimizing the following functional $\Delta[t]$ using the steepest descent method,

$$\Delta[t(r)] = \int d\mathbf{r} \left[\frac{\partial c(r, \rho_0)}{\partial \rho_0} - t(r) t_C(r) \right]^2, \quad (\text{B22})$$

where the function t_C is convolution of $t(\mathbf{r})$,

$$t_C(\mathbf{r}) = \int t(\mathbf{r} - \mathbf{r}') t(\mathbf{r}') d\mathbf{r}'. \quad (\text{B23})$$

The functional derivative $\kappa[t(\mathbf{r})]$ of $\Delta[t(\mathbf{r})]$ with respect to function $t(\mathbf{r})$ is

$$\begin{aligned} \kappa[t(\mathbf{r})] &= \frac{\delta \Delta[t]}{\delta t(\mathbf{r})} = -2 \left[\frac{\partial c(r, \rho_0)}{\partial \rho_0} - t(\mathbf{r}) t_C(\mathbf{r}) \right] t_C(\mathbf{r}) \\ &\quad - 4\ell(\mathbf{r}), \end{aligned} \quad (\text{B24})$$

where the function $\ell(r)$ is obtained as

$$\begin{aligned} \ell(\mathbf{r}) &= \int d\mathbf{r}' \left[\frac{\partial c(r', \rho_0)}{\partial \rho_0} t(\mathbf{r} - \mathbf{r}') t(\mathbf{r}') - t(\mathbf{r} - \mathbf{r}') t^2(\mathbf{r}') t_C(\mathbf{r}') \right]. \end{aligned} \quad (\text{B25})$$

The minimization of $\Delta[t(r)]$ by searching convergence of $\Delta[t(r)]$ through the iterative approach,

$$t_{n+1} = t_n + \lambda \kappa_n(t(\mathbf{r})). \quad (\text{B26})$$

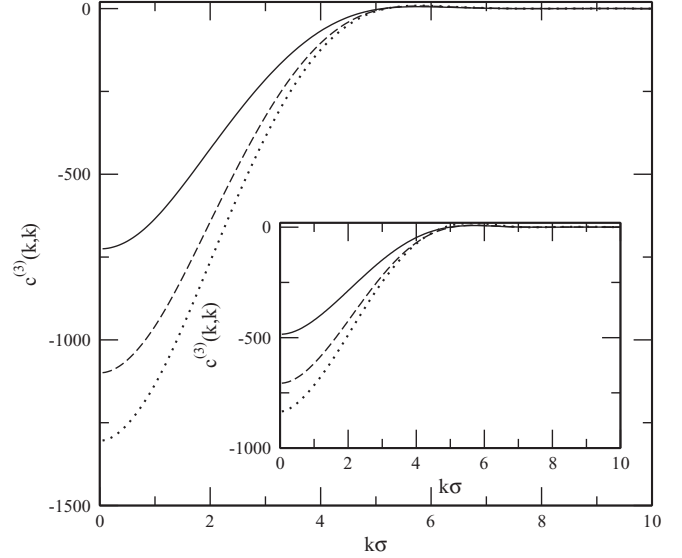


FIG. 5. The three-point function $c^{(3)}(\mathbf{k}, \mathbf{k})$ vs. $k\sigma$ shown for $\eta = .570$ (solid), $\eta = 0.596$ (dashed), and $\eta = 0.607$ (dotted). Inset shows corresponding results at those densities shown in the main panel with the Rogers-Young structure factor.

The gradient $\kappa_n[t(\mathbf{r})]$ is calculated with n th iteration $t(\mathbf{r})$. The parameter λ is taken so as to minimize the functional $\Delta[t(\mathbf{r})]$. The convergence criterion has been set by using

$$\left[\frac{\partial c(r)}{\partial \rho_0} - t(\mathbf{r}) t_C(\mathbf{r}) \right]^2 \leq 10^{-5} \left| \frac{\partial c(r)}{\partial \rho_0} \right|^2, \quad (\text{B27})$$

$$|t_{n+1} - t_n|^2 \leq 10^{-8}. \quad (\text{B28})$$

The two-point function $c^{(2)}(r)$ is obtained here by using both the Percus-Yevick [20] solution and the Bridge function method with the Rogers-Young approximation [21]. The corresponding value of $\partial c^{(2)}(r, \rho_0) / \partial \rho_0$ is substituted in Eq. (B9). Once $t(r)$ is known, the three-point direct correlation function $c^{(3)}(\mathbf{r}, \mathbf{r}')$ is calculated using the relation (B12). With azimuthal symmetry, the three-point direct correlation function $\tilde{c}^{(3)}(\mathbf{k}, \mathbf{k}')$ depends on k , k' , and $\cos \theta$ where θ is the angle between $\{\mathbf{k}, \mathbf{k}'\}$. In Fig. 1 we have shown the plot of ternary function $t(r)$ vs. distance r in units of σ for packing fraction $\eta = .594$ (.554) in the main panel (inset) with the corresponding two-point structure function taken from the Percus-Yevick approximation [20] (Rogers-Young structure factor [21]). The plot of $\tilde{c}^{(3)}(\mathbf{k}, \mathbf{k})$ is displayed in Fig. 5 for both the Percus-Yevick (main panel) and the Rogers and Young (inset) structure factors corresponding to three different packing fractions $\eta = .570$, .596, and .607.

[1] A. Cavagna, *Phys. Rep.* **476**, 51 (2009).

[2] Y. Singh, J. P. Stoessel, and P. G. Wolynes, *Phys. Rev. Lett.* **54**, 1059 (1985).

[3] T. Odagaki, *J. Phys. Soc. Jpn.* **86**, 082001 (2017).

[4] T. R. Kirkpatrick and D. Thirumalai, *Phys. Rev. B* **36**, 5388 (1987)

[5] T. Castellani and A. Cavagna, *J. Stat. Mech.* (2005) P05012.

[6] T. R. Kirkpatrick and D. Thirumalai, *J. Phys. A: Math. Gen.* **22**, L149 (1989).

- [7] R. Monasson, *Phys. Rev. Lett.* **75**, 2847 (1995).
- [8] J.-M. Bomont, J.-P. Hansen, and G. Pastore, *J. Chem. Phys.* **141**, 174505 (2014).
- [9] L. Angelani and G. Foffi, *J. Phys.: Condens. Matter* **19**, 256207 (2007).
- [10] F. Sciortino and P. Tartaglia, *Phys. Rev. Lett.* **86**, 107 (2001).
- [11] M. Cardenas, S. Franz, and G. Parisi, *J. Chem. Phys.* **110**, 1726 (1999).
- [12] M. Mézard and G. Parisi, *Phys. Rev. Lett.* **82**, 747 (1999).
- [13] W. Kauzman, *Chem. Rev.* **43**, 219 (1948).
- [14] S. Wu, J. Schmalian, G. Kotliar, and P. G. Wolynes, *Phys. Rev. B* **70**, 024207 (2004).
- [15] D. J. Amit and D. V. I. Roginsky, *J. Phys. A* **12**, 689 (1979).
- [16] S. Franz and J. Hertz, *Phys. Rev. Lett.* **74**, 2114 (1995).
- [17] C. Kaur, and S. P. Das, *Phys. Rev. Lett.* **86**, 2062 (2001).
- [18] J. D. Bernal, *Proc. R. Soc. Lond. Ser. A* **280**, 299 (1964).
- [19] J. L. Barrat, J. P. Hansen, and G. Pastore, *Mol. Phys.* **63**, 747 (1988).
- [20] J. K. Percus, and G. J. Yevick, *J. Phys. Rev.* **110**, 1 (1958).
- [21] F. J. Rogers, and D. A. Young, *Phys. Rev. A* **30**, 999 (1984).
- [22] S. P. Das, *Statistical Physics of Liquids at Freezing and Beyond* (Cambridge University Press, New York, 2011).
- [23] G. Parisi and F. Zamponi, *J. Chem. Phys.* **123**, 144501 (2005).
- [24] S. P. Das, *Rev. Mod. Phys.* **76**, 785 (2004).
- [25] U. Bengtzelius, W. Götze, and Sjolander, *J. Phys. C* **17**, 5915 (1984).
- [26] S. P. Das, and G. F. Mazenko, *Phys. Rev. A* **34**, 2265 (1986); *Phys. Rev. E*, **79**, 021504 (2009).
- [27] S. P. Das, *Phys. Rev. A* **42**, 6116 (1990).
- [28] J.-L. Barrat, and A. Latz, *J. Phys. Condens. Matter* **2**, 4289 (1990).
- [29] G. Szamel, *Europhys. Lett.* **91**, 56004 (2010).
- [30] T. Rizzo, *Phys. Rev. E* **87**, 022135 (2013).
- [31] G. I. Menon and C. Dasgupta, *Phys. Rev. Lett.* **73**, 1023 (1994).
- [32] S. Franz and G. Parisi, *Phys. Rev. Lett.* **79**, 2486 (1997).
- [33] H. Jacquin and F. Zamponi, *J. Chem. Phys.* **138**, 12A542 (2013).
- [34] T. R. Kirkpatrick, P. G. Wolynes, *Phys. Rev. A* **35**, 3072 (1987).
- [35] G. Parisi and F. Zamponi, *Rev. Mod. Phys.* **82**, 789 (2010).
- [36] J. Kurchan, G. Parisi, and F. Zamponi, *J. Stat. Mech.* (2012) P10012.
- [37] P. Charbonneau, J. Kurchan, G. Parisi, P. Urbani, and F. Zamponi, *Nat. Commun.* **5**, 3725 (2014).
- [38] P. Charbonneau, J. Yuliang, G. Parisi, and F. Zamponi, *Proc. Natl. Acad. Sci. USA* **111**, 15025 (2014).
- [39] S. A. Brazovskii, *Sov. Phys.-JETP* **41**, 85 (1975).
- [40] S. P. Das, *Phys. Rev. A* **36**, 211 (1987).
- [41] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Elsevier Academic Press, San Diego, CA, 2006).
- [42] T. V. Ramakrishnan and M. Yussouff, *Phys. Rev. B* **19**, 2775 (1979).
- [43] L. L. Lee, *J. Chem. Phys.* **60**, 1197 (1974).
- [44] G. B. Arfken and H. J. Weber, *Mathematical Methods for Physicists*, 6th ed. (Elsevier Academic Press, Amsterdam, 2005).