Metastable structures with modified weighted density-functional theory

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The free energy of the supercooled liquid near freezing is studied in the density-functional approach using the modified weighted density approximation. A class of minima corresponding to heterogeneous structures characterized by weak mass localization are detected. The stability of these structures is found to be greater than the highly localized ''hard-sphere glass'' state in the intermediate density range above freezing.

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I. INTRODUCTION

The study of the amorphous state of a liquid, which is supercooled below its characteristic freezing point, has been an area of much current research interest. Various theoretical approaches have evolved during the last two decades to understand the behavior of a liquid in the supercooled or glassy state. Traditionally, the identification of these states has been associated with the sharp change in the macroscopic dynamical properties such as diverging viscosity or vanishing diffusion coefficients. The dynamical features of this state have been studied from the analysis of the equations of nonlinear fluctuating hydrodynamics [1,2] as well as using a kinetic theory [3–5] approach. These models have achieved a fair amount of success in attaining agreement with the experimental observations. The other approach to the study of glassy systems was through the analysis of thermodynamic properties of the metastable states. Interestingly, landscape paradigms have been used for the study of a wide class of complex systems in recent years [6]. Generally a glassy system has a complicated landscape with many possible states and qualitative behaviors of such systems are explored [7] through an analysis of the same. In the present paper we consider the equilibrium thermodynamic property, namely, the free energy of the system in the supercooled state. The glassy state is also characterized by nonequilibrium properties such as aging and to what extent the changes are prompted by an underlying phase transition is still a matter of current research. However, for studying the nature of metastable states, ideas of the equilibrium statistical mechanics are often used. In this respect, the free-energy landscapes for disordered systems such as spin glass [8,9] have been done. In the case of supercooled liquids, the scenario for the structural glass transition was discussed by Kirkpatrick and Wolynes [10] using such concepts. The thermodynamic property is studied in the density-functional approximation, which involves evaluating the free energy for a particular density profile that may be inhomogeneous like to a crystal or homogeneous like a uniform liquid. The metastable and stable structures are studied [11–16] by identifying the existence of free-energy minima for a specific system including amorphous structures.

The density-functional theory has gained wide acceptance over the past two decades as a fruitful approach to study the freezing transitions and other physical properties of inhomogeneous classical fluids. It provides the tools to qualitatively gain insight into the structural changes that a system undergoes when it is compressed to high densities. The basic principle that governs this theory is based on the theorem established by Mermin [17] according to which, once the interparticle potential of a system is specified, there exists a one-to-one correspondence between the external potential and the one particle density distribution function $\rho(\vec{r})$. The thermodynamic potentials of the system besides being a function of other thermodynamic variables, are also functional of the external potential. As a consequence of Mermin's theorem, these thermodynamic potentials can be expressed as a functional of the local density $\rho(\vec{r})$. Thus, this study involves the investigation of the free-energy landscape as a functional of the density distribution. The thermodynamic variational principle is applied to minimize the free-energy functional, and hence, identify the stable and metastable phases of the given system [18]. The minimization is generally carried out in a constrained manner by supplying the underlying lattice structure as the input. For a system of classical particles, the stationary solution of the dynamical equations for the one-particle distribution function, e.g., the Revised Enskog Equation [19], also corresponds to the local minima of the same free-energy functional of density that determines the equilibrium states [20].

The hard-sphere model approximates well the structure of dense particle systems since short-range interparticle repulsion is the major effect in determining the structure. For a hard-sphere system compressed to high density, the isotropic fluid undergoes transition to a fcc (face-centered-cubic) crystal corresponding to a freezing density $\rho_f^* = 0.95$. However, metastable states of such a system are also observed if freezing is avoided. Singh *et al.* pioneered the use of the density-functional theory (DFT) [11] in discovering the existence of a ''hard-sphere glass'' state as a metastable free-energy minima pertaining to the Bennett's amorphous structure. This study was motivated to determine the structural aspects of glassy states from a purely thermodynamical approach. The corresponding metastable state is a highly localized density distribution which is unlikely to associate with supercooled states at intermediate densities. More results pointing towards the existence of similarly localized structures were reported thereafter, by using the nonperturbative forms of the free-energy functional [12,14]. In a recent paper reported by the present authors [16], a free-energy minima characteristic of a structure with a weakly localized, heterogeneous density profile was found apart from the usual ''hard-sphere glass''

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found in the earlier works. This study was done using the Ramakrishnan-Yussouff (RY) form of the free-energy functional [21]. Here, a key approximation used in earlier works in evaluating the entropic part of the free energy was avoided. The amount of localization specific to this state was found to be conforming with the observed computer-simulation results. However, this method involved expressing the excess part of the free energy as a perturbation expansion around the liquid state of the same average density and since this expansion is generally truncated at the second order, the qualitative correctness of its results are ambiguous for the *highly localized* structures in which the deviation of the one-particle density $\rho(\vec{r})$ from the average solid density ρ is very large. In order to avoid such approximations, various nonperturbative methods have evolved beginning with the weighted density-functional theory of Tarazona [22]. Subsequently, this was studied by Curtin and Ashcroft [23] and Denton and Ashcroft [24] who devised the modified weighted density approximation (MWDA). This approach involves the global mapping of the inhomogeneous system specified by $\rho(\vec{r})$, into a homogeneous fluid system of density $\hat{\rho}$ that has the similar strength of correlations as that of the inhomogeneous system. In the present paper, we have explored the metastable character of the weakly localized amorphous structures relative to the ''hard-sphere glass'' state by employing the MWDA technique. In this paper, we illustrate the presence of both the free-energy minima as evaluated by the *exact* calculation of the two competing terms of the free-energy functional. The results display a quantitative change in the free-energy values as calculated using the RY functional [16], and hence, affect their relative metastable character. We observe that the amorphous state prefers the weakly localized density structure for lower and intermediate densities. In the higher-density ranges, the highly localized structure becomes more stable. These features are observed by considering different distributions for the amorphous lattice points [12,14].

The paper is organized as follows: In Sec. II, we discuss the computational details of the free-energy model considered. We briefly review the MWDA technique and illustrate the evaluation of the ideal-gas part and the excess part of the free energy for the random structure. The following section, Sec. III, contains the explicit results observed using these techniques, and in Sec. IV, the implications of these results are discussed.

II. MODEL FOR THE FREE-ENERGY FUNCTIONAL

The formulation of all density-functional theories begins with the definition of the ensemble averaged, one-particle density distribution $\rho(\vec{r})$ for the inhomogeneous structure. One very successful prescription for this was first put forward by Tarazona [22] who expressed the $\rho(\vec{r})$ as a summation over the lattice sites of normalized isotropic Gaussian distribution functions. The formal expression being

$$\rho(\vec{r}) = \sum_i \phi(|\vec{r} - \vec{R}_i|), \qquad (1)$$

where the amorphous lattice sites are denoted by $\{\vec{R}_i\}$ and the function ϕ is taken as the isotropic Gaussian $\phi(r) = (\alpha/\pi)^{3/2} e^{-\alpha r^2}$. The parameter α is inversely proportional to the square of the width of each Gaussian peak and thus its low value depicts a loosely bound particle to the lattice site. In fact, the $\alpha \to 0$ limit represents the liquid or the homogeneous state and larger values depict a highly localized solid structure. The minimization of the free-energy functional is effectively conducted with respect to α at a given density ρ and the value of α corresponding to the minimum free energy points towards the phase of the system in equilibrium. The correctness of this simple Gaussian approximation has been tested by various authors who have used its more complicated, basically anisotropic forms and have found the freezing results to be rather insensitive to this variation [25,26]. The root-mean-square displacement associated with any particle in the system can be estimated by the α value corresponding to the minimum free energy. In many freezing studies, this has formed the basis for prediction of the Lindemann ratio characteristic of the crystal structure.

The Helmholtz free-energy functional is evaluated using this density distribution function Eq. (1). In general, the free energy can be written as a sum of the ideal-gas contribution $F_{id}[\rho(\vec{r})]$, and the excess part $F_{ex}[\rho(\vec{r})]$, as $F[\rho] = F_{id}[\rho] + F_{ex}[\rho]$. Here, F_{id} is the entropic contribution, due solely to the packing of the system, whereas the excess part quantifies the interaction part of the free energy. The free-energy minima are determined by the competition between these two terms. The ideal-gas part of the free-energy functional of an inhomogeneous system is given as (in units of β^{-1})

$$F_{id}[\rho(\vec{r})] = \int d\vec{r}\, \rho(\vec{r}) \{\ln[\wedge^3 \rho(\vec{r})] - 1\}, \qquad (2)$$

$\wedge$ being the thermal wavelength. For considering the minimization in larger ranges of the width parameter α corresponding to very localized density distributions, the entropic part per particle f_{id}, is generally approximated by the expression

$$f_{id}[\rho] \approx \left[-\frac{5}{2} + \ln \wedge^3 \left(\frac{\alpha}{\pi} \right)^{3/2} \right]. \qquad (3)$$

Equation (3) is obtained from the general expression (2) by approximating the summation over all lattice sites in $\rho(\vec{r})$ by counting the contribution from just the nearest site. This is valid for large α (greater than ≈ 40), since for such large values the Gaussian profile is so narrow that there is no overlapping between those centered around different sites. The earlier studies conducted in this respect [11,12,14], used this form of f_{id} to calculate the ideal-gas part of the free energy. To investigate the existence of metastable states characterized by loosely bound particles that are actually seen in the computer simulation studies, the free-energy landscape needs to be explored in the lower ranges of α and thus we evaluated this term exactly as

$$f_{id}[\rho(\vec{r})] = \int d\vec{r}\, \phi(\vec{r}) \left[\ln\left(\wedge^3 \int d\vec{R}\, \phi(\vec{r} - \vec{R})[\delta(\vec{R}) \right. \right.$$
$$\left. \left. + \rho g(\vec{R})] \right) - 1 \right], \tag{4}$$

where $g(\vec{R})$ is the site-site correlation function characteristic of the random structure used. In the earlier work [16], it was shown that this expression starts matching with the asymptotic result for $\alpha > 20$ within a 5% error. This formulation takes proper account of the wide, overlapping Gaussian distribution functions specific to systems with lower α values.

Following the Ramakrishnan-Yussouff formulation of the interaction part of the free energy of the inhomogeneous system, various new methodologies have evolved in the past decade. Although all density-functional theories approximate the solid as a strongly inhomogeneous fluid, they generally differ in formulating this approximation. In the present paper, we have used the MWDA to evaluate the interaction part of the free energy. This theory involves the global mapping of the inhomogeneous system specified by $\rho(\vec{r})$, into an effective or equivalent homogeneous fluid of density $\hat{\rho}$ that has the similar level of correlations as that of the inhomogeneous system. The density $\hat{\rho}$ of this liquid is called the weighted density of the solid and can be obtained as

$$\hat{\rho} = \frac{1}{N} \int d\vec{r}_1 \rho(\vec{r}_1) \int d\vec{r}_2 \rho(\vec{r}_2) w(\vec{r}_1 - \vec{r}_2; \hat{\rho}), \tag{5}$$

where $w(r)$ is a normalized weight function obtained by equating the direct correlation function of the homogeneous system $c(r;\hat{\rho})$ to the second functional derivative of the excess free energy of the solid. The excess free energy of the solid is approximated as

$$F_{ex}[\rho] = N f_{ex}(\hat{\rho}), \tag{6}$$

where $f_{ex}(\hat{\rho})$ is the excess free energy per particle of the homogeneous state corresponding to the weighted density of the inhomogeneous system. A self-consistent integral equation for the weighted density is obtained by following the above prescription [24]. For the random structure, this can be reformulated as

$$2 f'_{ex}(\hat{\rho})\hat{\rho} = -\rho \hat{\rho} f''_{ex}(\hat{\rho}) - \int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{R}\, c(|\vec{r}_1$$
$$- \vec{r}_2|; \hat{\rho}) \phi(\vec{r}_1 - \vec{R}) \phi(\vec{r}_2)[\delta(\vec{R}) + \rho g(\vec{R})]. \tag{7}$$

This expression can be further reduced to the following form:

$$2 f'_{ex}(\hat{\rho})\hat{\rho} = -\rho \hat{\rho} f''_{ex}(\hat{\rho}) + \alpha \sqrt{\frac{2\alpha}{\pi}} I_1(\alpha)$$
$$+ 4\rho \sqrt{\frac{\pi\alpha}{2}} \int_0^\infty dR\, R\, g(R) I_2(\alpha; R), \tag{8}$$
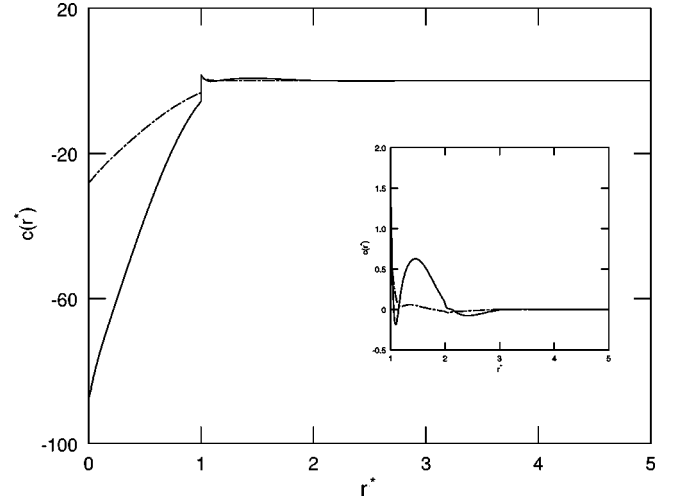

FIG. 1. Direct correlation function of the homogeneous state $c(r)$ evaluated as the analytic solution of the Percus-Yevick integral equation for hard spheres with Verlet-Weis correction added. Solid line is $c(r^*)$ at $\rho^* = 0.8$ and dashed line is at $\rho^* = 1.02$. The distance r is expressed in units of σ ($r^* = r/\sigma$) and the density in units of σ^{-3} ($\rho^* = \rho\sigma^3$).

where I_1 and I_2 are the integrals defined as

$$I_1(\alpha) = \int_0^\infty dt\, t^2 c(t) e^{-(\alpha t^2/2)} \tag{9}$$

and

$$I_2(\alpha; R) = \int_0^\infty dt\, t\, c(t)[e^{-[\alpha(t-R)^2]/2} - e^{-[\alpha(t+R)^2]/2}]. \tag{10}$$

Here, the derivative with respect to density is denoted as f'_{ex} i.e., $f'_{ex} = \partial f_{ex}/\partial_\rho$. Equation (8) is solved iteratively to obtain the $\hat{\rho}$ at a given average density ρ and width parameter α.

III. RESULTS

The self-consistent equation for the density $\hat{\rho}$ of the homogeneous liquid to which the inhomogeneous state is mapped involves the direct correlation function for the liquid. Thus, the homogeneous state free energy $f_{ex}(\rho)$, and hence, the direct correlation function of the liquid state $c(r)$ form a significant building block of this theory. In Ref. [16], as well as the present paper, we have used a fairly accurate form of $c(r)$ given by the solution of the Percus-Yevick equation with the Verlet-Weis correction added [27,28]. The homogeneous state excess free energy $f_{ex}(\rho)$ should also be self-consistent with the form of the $c(r)$ used. Thus, the Carnahan-Starling formula is used in computing both the excess free energy [29] of the homogeneous liquid, as well as the direct correlation function. In Fig. 1, we have shown the $c(r^*)$ at density $\rho^* = 1.02$ as the solid line, and the dashed line shows the $c(r^*)$ at $\rho^* = 0.8$ for comparison with the result of Henderson and Grundke [28]. We use the hard-sphere diameter σ as the unit of length in this paper and the

quantities r^* and ρ^* correspond to dimensionless numbers r/σ and $\rho\sigma^3$, respectively. The tail of $c(r)$ is significant to take into account with increasing density since the correlations become longer ranged with increasing ρ and the Percus-Yevick $c(r)$ ignores this tail part. To study the role of $c(r)$, we have also tested these theories by using different approximations for $c(r)$. The existence of the weakly localized minima is observed with any $c(r)$ and a self-consistent form of $f_{\text{ex}}(\rho)$. However, its relative metastable character is quite sensitive to the accuracy of the liquid state information supplied in the specific density range. For higher ranges of the width parameter α, the average density of the corresponding highly localized solid is much higher than the density $\hat\rho$ of the equivalent liquid with a similar level of correlation. Thus, the inhomogeneous solid is mapped to a liquid of much lower density where the Percus-Yevick model for $c(r)$ gives an accurate description of the correlation. In the region of our interest, i.e., small α, due to the weakly localized Gaussian profiles, the average density of the inhomogeneous system comes close to that of the mapped liquid. As a result of this, a more accurate description of the direct correlation function and the free energy is required at such higher densities to obtain more reliable results.

Another important input in these calculations is the underlying lattice structure around which the Gaussian profiles are centered. The structural description of the underlying amorphous lattice is provided through the site-site correlation function $g(\vec{R})$ of the Bernal's random structure [30] that is generated through the Bennett's algorithm [31]. Following Baus and Colot [12], we use the scaling relation for $g(R)$ to parametrize a given structure in the following form:

$$g(R,\eta) = g_B\left[R\left(\frac{\eta}{\eta_o}\right)^{1/3}\right], \qquad (11)$$

where η denotes the average packing fraction. Here, η_o is used as a scaling parameter for the structure [12,14], such that at $\eta=\eta_o$, the structure corresponds to Bernal packing. Increasing values of η_o denote an increasingly separated or loose underlying lattice structure. For evaluating the free energy in the relatively smaller ranges of the width parameter, the R integration, i.e., summation over lattice sites, cannot be truncated at the first coordination shell, as has been done in previous calculations. Here, the Gaussians at different lattice sites are overlapping, and thus convergence of the integrals is obtained at very high R values. Thus, $g(R)$ is formulated in an analytical form by fitting the data available from Bennett's paper [31] and then extrapolating it to higher R values.

Using the MWDA formulation of free energy, we have studied the thermodynamic properties of the heterogeneous amorphous structures. A type of metastable state is detected apart from the usual "hard-sphere glass" as a separate distinct minimum on the free-energy landscape. The density distribution is given by overlapping Gaussian profiles centered on a random lattice with the width parameter α in the lower ranges in comparison to the corresponding values for the hard-sphere glass. This is illustrated in Fig. 2, where both the minima observed for the Bernal's random structure are shown. This figure corresponds to the amorphous structure at
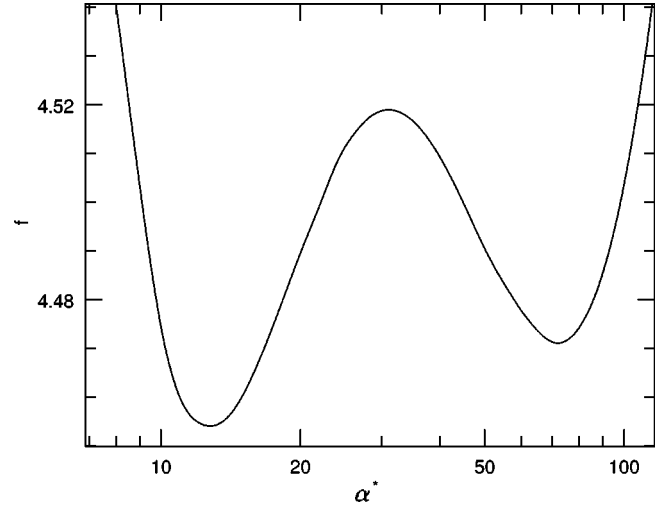

FIG. 2. Free energy per particle f (in units of β^{-1}) vs width parameter α^* ($\alpha^*=\alpha\sigma^2$) at $\rho^*=1.02$, $\eta_o=0.70$.

density $\rho^*=1.02$ and $\eta_o=0.70$. The lower free energy is attributed to the structure with density distribution characterized by $\alpha^*=13$, which represents a much more loosely bound structure than that corresponding to the higher free-energy minima at $\alpha^*=72$. We find that the weakly localized minimum only exists when the underlying lattice structure is random and is absent for the crystalline structure with long-range order. Only the highly localized minimum is observed in the case of fcc structure. In Fig. 3, this feature is depicted where the free energy per particle f versus density ρ^* is shown at $\eta_o=0.70$, for both types of structures. The solid line corresponds to the weakly localized state and the dashed line represents the "hard-sphere glass" state. The free energy of the heterogeneous state is lower than that of the "hard-sphere glass" up to $\rho^*\approx1.03$ and for densities greater than that this trend reverses. Here, we would like to indicate that both the inhomogeneous structures for high and low α are
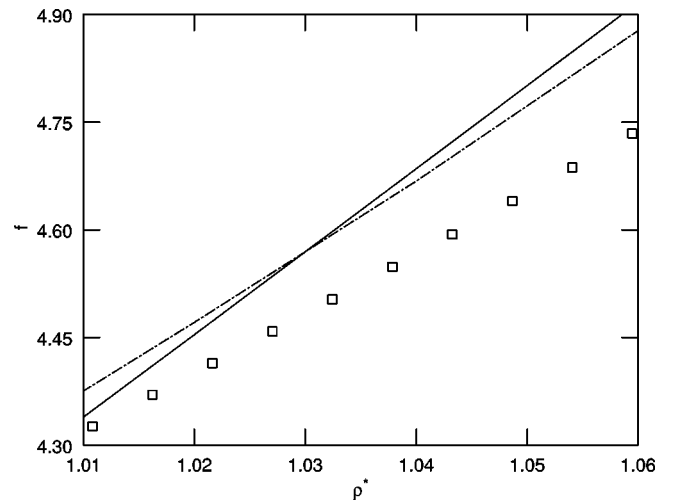

FIG. 3. Free energy per particle (f) (in units of β^{-1}) vs average density ρ^* at $\eta_o=0.70$. The solid curve corresponds to the weakly localized state and the "hard-sphere glass" state is shown as the dashed line. The squares denote f_{fcc}.
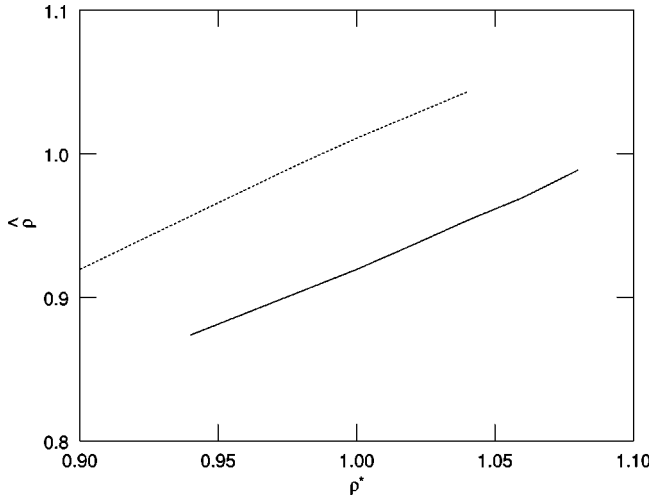
FIG. 4. Variation of weighted density $\hat{\rho}$ with the average density ρ^*. The solid line represents the heterogeneous structure at $\eta_o = 0.70$ and the dashed line is for $\eta_o = 0.66$.

more stable than the uniform liquid state. The free energy per particle of the fcc structure calculated using the Verlet-Weis $c(r)$ is also shown by the square symbols. It should be noted that with the present choice of the structure factor, the density at which the fcc structure becomes more stable than the liquid occurs at $\rho = 0.946$ corresponding to the freezing density.

In general, for the face-centered cubic crystal, the weighted density $\hat{\rho}$ is found to be lower than the corresponding average density of the crystal ρ. $\hat{\rho}$ monotonically decreases with the increase of ρ and it is only in the very high-density regions ($\eta > 0.63$ [32]), that a reversal of this trend has been observed. On the other hand, in the case of the class of minima for low α as in the present paper, $\hat{\rho}$ is even higher than the average density ρ of the inhomogeneous structure. This is seen for underlying amorphous lattice structures corresponding to values of the parameter η_o ($\leqslant 0.66$). For the structures corresponding to higher η_o values, this trend does not exist and we have based the inferences of this paper from such structures only. In Fig. 4, we have shown this fact by illustrating the variation of $\hat{\rho}$ with ρ for $\eta_o = 0.66$ (dashed line) and $\eta_o = 0.70$ (solid line).

Another feature observed in this calculation is that the free-energy minima corresponding to highly localized density profiles termed as the hard-sphere glass, disappear for certain densities. This is shown in Fig. 5 at $\rho^* = 0.98$ at $\eta_o = 0.70$. Here, for the whole range of the density considered, the lower α minima is distinctly present but the corresponding one in the higher α ranges gets smeared off at lower densities. We observe that there is a crossover value of the average density ρ, denoted as ρ_c^* below which only the minimum in the lower range of α is observed. This aspect is not observed [14] when the Percus-Yevick result for the direct correlation function $c(r)$ is used. The more accurate description of the correlations developing at high density being included in the present calculation is likely to be the reason for this observation. Furthermore, with the increasing value of the parameter η_o, this value of ρ_c^* keeps increasing as shown in Fig. 6.
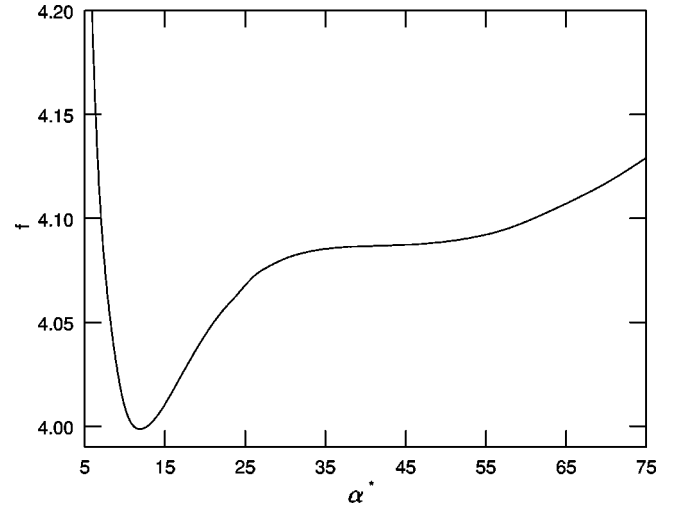

FIG. 5. Free energy per particle f (in units of β^{-1}) vs width parameter α^* at $\rho^* = 0.98$, $\eta_o = 0.70$. Only the heterogeneous minimum is present in the free-energy landscape.

The width parameter α is a measure of the strength with which the particles are pinned to their respective sites in their equilibrium (or quasiequilibrium) state. It is inversely proportional to the root-mean-square displacement of the particles from their sites. This also defines the Lindemann ratio. As was already indicated in Ref. [16], LaViolette and Stillinger [33] have observed that the root-mean-square displacement of the particles in the supercooled states is approximately three times more than that found in the crystal structure at freezing. We observed in Ref. [16] the same value for this ratio corresponding to the weakly localized state using the RY functional technique. In the present paper, with an entirely different formulation, a similar relation is found to be true again. This is shown in Fig. 7, where we plot the parameter d defined as $d = 1/\sqrt{\alpha}$, for both the heterogeneous (solid line) and the hard-sphere glass minimum (dashed line) with respect to density ρ^*. This is shown here with $\eta_o = 0.70$ for the amorphous structure. The corresponding values for the fcc hard-sphere crystal are shown as
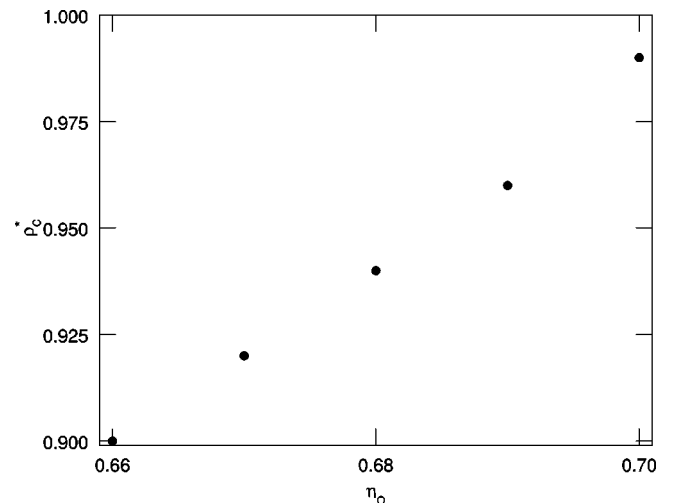

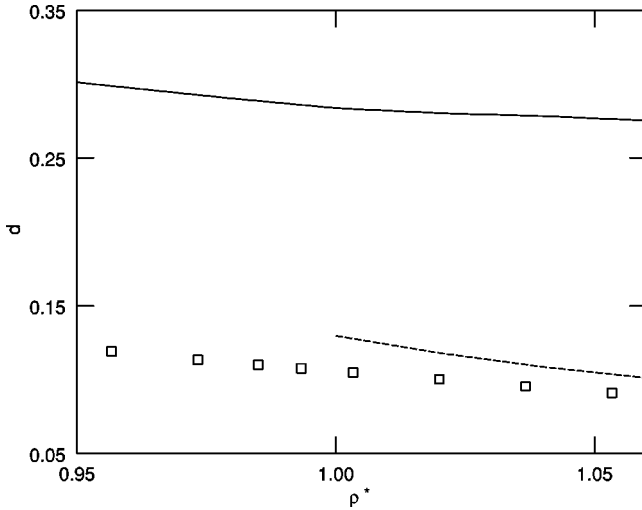FIG. 6. Variation of the ρ_c^* (see text) with respect to η_o.

FIG. 7. The root-mean-square displacement d (in units of σ) vs density ρ^*. The solid curve illustrates results for the heterogeneous state and the dashed curve represents the "hard-sphere glass" state (both at $\eta_o = 0.70$). The squares represent the corresponding fcc values.

squares. The hard-sphere glass structure shows a localization close to that of a crystal. These features are observed universally at any η_o value.

Apart from the strength of localization, the thermodynamic features of this weakly localized state can also be computed from this study. The pressure of the hard-sphere liquid is obtained from the expression

$$\beta P = \rho \frac{\partial f}{\partial \rho} - f. \tag{12}$$

For the weakly localized state, the pressure computed in this way is, in general, higher than that corresponding to the "hard-sphere glass" state. In Fig. 8, we have shown the pres-
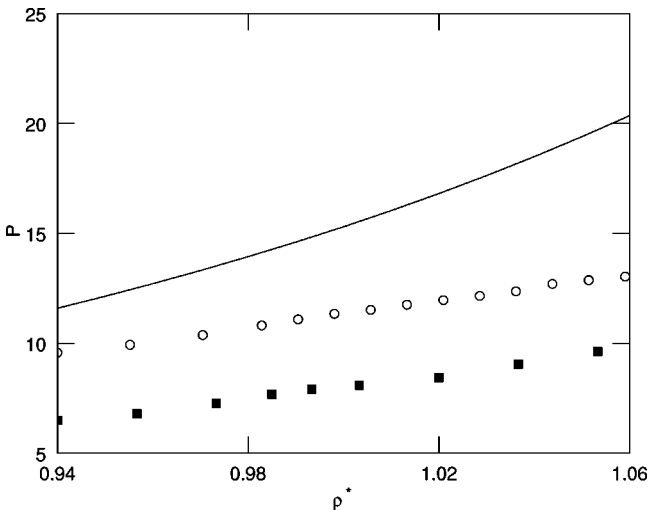

FIG. 8. Pressure P [in units of $(\beta\sigma^3)^{-1}$] vs density ρ^* for the weakly localized state is shown as circles. The corresponding results for the fcc structure are shown with filled squares while the same for the homogeneous liquid state is shown with the solid line.

sure P, evaluated for the low α minima (shown as circles). The derivatives, with respect to the density involved in this computation, were obtained numerically from results for the free energy calculated within the MWDA approximation. The numerical result is sensitive to the form of the direct correlation function used. Thus, if the tail part in $c(r)$, signifying longer-range correlation in the fluid, is ignored—it results in a more steep increase of the corresponding pressure with density. In the same figure we also show the corresponding curve for the homogeneous liquid (solid line) and the fcc state (squares).

IV. DISCUSSION

We have presented here the detailed description of a calculation, which identifies a heterogeneous metastable state as a minimum in the free-energy landscape of a given random structure. This state was identified in our earlier work [16] using the RY functional formulation of the density-functional theory. It was shown there that this state could be identified with the metastable supercooled liquid states. The average particle displacement in the weakly localized states conformed with the computer simulation predictions of LaViolette and Stillinger [33]. The present paper is based on a nonperturbative approximation of the interactive part of free-energy functional. The significance of this paper lies in strengthening the earlier finding by arriving at similar qualitative results related to the identification of the weakly localized state. This study could also be used here to compute other thermodynamical properties such as pressure in this state [34]. The observation that the root-mean-square displacement is similar to what is seen in computer simulations demonstrates that the class of minima are useful in describing the metastable state in the first stage of supercooling. Here, η_o is being used as a parameter so as to generate different random structures through the scaling of the Bernal's random structure. The increasing values of η_o at the same η, refer to a more dispersed random structure, as is apparent from Eq. (11). When η_o is equal to 0.64 the resulting structure is identical to the Bernel close-packed structure.

For the crystal, the free-energy minima lie in the large α range. The RY formulation is expressed as a truncation at the second order of the perturbation expansion in density. For density distribution corresponding to large α values, in general the deviation $\delta\rho(\vec{r}) = \rho(\vec{r}) - \rho$ is very large and thus truncating the expansion at the second order is an over approximation. On the other hand, the MWDA formulation approximates the properties of the inhomogeneous structure by that of an *equivalent* liquid. Since the free-energy minima for ordered structures lie in the larger ranges of α, the corresponding density of the *equivalent* liquid is much less than that of the inhomogeneous structure. Thus, the fairly well-known liquid state description in the lower and intermediate density regions, like the Percus-Yevick approximation could be used reliably. Hence, for hard-sphere systems, this theory has been considerably successful in determining the freezing parameters of the liquid-crystal transition. This has been the particular advantage of the MWDA approach in studying the stability of highly localized structures. On the other hand,

due to the overlapping density profiles in the low α region, the corresponding $\hat{\rho}$ is close to that of the average density ρ.

This paper highlights the existence of heterogeneous structures that are more stable than the highly localized amorphous structures in the relatively lower and intermediate densities for the supercooled liquid for supercooled densities closer to the freezing point. A subsequent step to understanding the nature of the metastability would require a proper study of the dynamics associated with the system around these metastable states and obtain an estimation of the relaxation to these states.

[1] B. Kim and G. F. Mazenko, Adv. Chem. Phys. **78**, 129 (1990).

[2] S. P. Das and G. F. Mazenko, Phys. Rev. A **34**, 2265 (1986); S. P. Das, *ibid.* **36**, 211 (1987).

[3] U. Bengtzelius, W. Götze, and A. Sjölander, J. Phys. C **17**, 5915 (1984).

[4] W. Götze and L. Sjögren, Z. Phys. B: Condens. Matter **65**, 415 (1987).

[5] C. Z. Liu and I. Oppenheim, Physica A **235**, 369 (1997); M. Manno and I. Oppenheim, *ibid.* **265**, 520 (1999).

[6] *Landscape Paradigms in Physics and Biology*, edited by H. Frauenfelder, A. R. Bishop, A. Garcia, A. Perelson, D. Sherrington, and P. Swart [special issue of Physica D **107**, 117(1997)].

[7] S. Sastry, P. G. Debenedetti, and F. H. Stillinger, Nature (London) **393**, 554 (1998).

[8] M. Mezard and G. Parisi, Phys. Rev. Lett. **82**, 747 (1999).

[9] G. Biroli, J. Phys.: Condens. Matter **12**, 6375 (2000).

[10] T. R. Kirkpatrick and P. G. Wolynes, Phys. Rev. A **35**, 3072 (1987).

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

[12] M. Baus and Jean-Louis Colot, J. Phys. C **19**, L135 (1986).

[13] R. W. Hall and P. G. Wolynes, J. Chem. Phys. **86**, 2943 (1987).

[14] H. Löwen, J. Phys. C **2**, 8477 (1990).

[15] C. Dasgupta, Europhys. Lett. **20**, 131 (1992).

[16] C. Kaur and S. P. Das, Phys. Rev. Lett. **86**, 2062 (2001).

[17] N. D. Mermin, Phys. Rev. **137**, A1441 (1965).

[18] T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959); R. Evans, Adv. Phys. **28**, 143 (1979).

[19] T. R. Kirkpatrick, Shankar P. Das, Matthieu H. Ernst, and J. Piasecki, J. Chem. Phys. **92**, 3768 (1990).

[20] James W. Dufty and Shankar P. Das, in *Strongly Coupled Coulomb Systems*, edited by Gabor J. Kalman, Martin P. Rommel, and Krastan B. Blagoev (Plenum Press, New York, 1998).

[21] T. V. Ramakrishnan and M. Yussouff, Phys. Rev. B **19**, 2775 (1979).

[22] P. Tarazona, Mol. Phys. **52**, 871 (1984).

[23] W. A. Curtin and N. W. Ashcroft, Phys. Rev. A **32**, 2909 (1985).

[24] A. R. Denton and N. W. Ashcroft, Phys. Rev. A **39**, 4701 (1989).

[25] R. Ohnesorge, H. Löwen, and H. Wagner, Europhys. Lett. **22**, 245 (1993).

[26] Jean-Louis Colot, M. Baus, and Hong Xu, Mol. Phys. **57**, 809 (1986).

[27] L. Verlet and J. J. Weis, Phys. Rev. A **45**, 939 (1972).

[28] D. Henderson and E. W. Grundke, J. Chem. Phys. **63**, 601 (1975).

[29] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).

[30] J. D. Bernal, Proc. R. Soc. London, Ser. A **280**, 299 (1964).

[31] Charles Bennett, J. Appl. Phys. **43**, 2727 (1972).

[32] A. R. Denton, N. W. Ashcroft, and W. A. Curtin, Phys. Rev. E **51**, 65 (1995).

[33] R. A. LaViolette and F. H. Stillinger, J. Chem. Phys. **83**, 4079 (1985); Frank H. Stillinger, Science **267**, 1935 (1995).

[34] J. P. Hansen and J. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1976).