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Heterogeneities in Supercooled Liquids: A Density-Functional Study

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A metastable state, characterized by a low degree of mass localization, is identified using density-functional theory (DFT). This free energy minimum, located through the proper evaluation of competing terms in the free energy functional, is independent of the specific form of the DFT used. Computer simulation results on particle motion indicate that this heterogeneous state corresponds to the deeply supercooled state.

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The properties of supercooled liquids are of much current interest and are being studied from different approaches related to their thermodynamic as well as dynamic aspects [1–6]. A normal liquid is characterized by a homogenous density, and when it is supercooled below the freezing transition it continues to stay in the amorphous phase. With the increase in density a solidlike phase is formed with the particles being localized around their mean positions on a random structure. The underlying lattice on which such localized motion takes place is related to the time scales of relaxation in the supercooled liquid. While the supercooled liquid starts to attain solidlike properties, structurally it does not have any long range order like the one present in a crystal. The heterogeneity in glassy systems over length and time scales has been studied in several recent works [7] related to computer simulations. Here we consider the heterogeneous density profile in the liquid and investigate the question of having metastable states in between the homogeneous liquid state and the regular crystalline state. The stability of such a structure has been studied in this work from a thermodynamic point of view, using the standard methods of density-functional theory (DFT). It provides the means to test if a given structure, i.e., a configuration of atoms is the "most" stable at a specified temperature and density. This method has generally been used [8–12] for the study of a liquid freezing into an ordered crystalline state through a first order transition.

In practical calculations of the DFT an explicit functional form for the inhomogeneous density function against which the free energy functional is tested is needed. One very successful prescription of density distribution is as a superposition of density profiles centered on a lattice,

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

where the $\{\vec{R}_i\}$ denotes the underlying lattice and the function ϕ is taken as the isotropic Gaussian $\phi(r) = (\frac{\alpha}{\pi})^{3/2} e^{-\alpha r^2}$ [10]. Here α is the variational parameter that characterizes the width of the peak, which represents the degree of localization of mass in the system. Thus the homogeneous liquid state is characterized by Gaussian profiles of very large width such that each provides the same contribution in the sum at all spatial positions. Singh *et al.* [13] have shown that the distribution of $\vec{R}_i$ over a random lattice determined from the Bernal packing [14] allows a minimum for the free energy. The state corresponding to this becomes more stable than the homogeneous liquid state for packing fraction $\eta > 0.59$. This is obtained for very large α that corresponds to an inhomogeneous and *highly localized* density distribution that has been termed as the "hard sphere glass." This metastable state, however, is not compatible with the experimental findings [5,6] which find the metastable supercooled state with a much lower degree of localization.

We have studied this through the various [8,11] formulations of the DFT for the density profiles centered around a random lattice that corresponds to a heterogeneous density distribution. Here we consider the density profiles that are *less* localized than the so-called hard sphere glass by evaluating the free energy of the system for α values that are *considerably smaller* than what was previously studied. We also consider the effects of fluctuations in the width around a mean value. The key result of this study is the observation of a free energy minimum where the density function corresponds to the small α region. This minimum is seen apart from the usual high α minimum, as reported in the earlier works [13,15,16].

The expression for the total free energy contains two parts—the ideal gas term and the interaction term, $F[\rho] = F_{\rm id}[\rho] + F_{\rm ex}[\rho]$. The ideal gas term of the free energy functional (in units of β^{-1}) is given by

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

Λ being the thermal wavelength. In the earlier works [13,15,16], where highly localized structures have been investigated, generally α was chosen to be large (greater than $\approx$50) and Eq. (2) was approximated by its asymptotic value for large α,

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

However, in the low α range where overlapping Gaussians from different sites contribute, we evaluate this term exactly from the computation of the integral given in (2) as

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

where $g(\vec{R})$ is the site-site correlation function which provides the structural description of the random structure used. We have used the Bernal's random structure [14] generated through the Bennett's algorithm [17]. We approximate the $g(\vec{R})$ as

$$g(\vec{R}) = g_B\left[R\left(\frac{\eta}{\eta_o}\right)^{1/3}\right], \quad (5)$$

where η denotes the average packing fraction and η_o is used as a scaling parameter for the structure [15,16] such that at $\eta = \eta_o$ Bernal's structure is obtained. The ideal free energy evaluated using this exact treatment, Eq. (4), is shown in Fig. 1 for $\rho_o = 1.0$. This agrees on extrapolation to the limit of the $\alpha \to 0$ [i.e., $\rho(\vec{r}) \to \rho_o$] result, i.e., -1. The exact evaluation starts approaching the asymptotic (large α) result (dashed line), for $\alpha > 20$ within 5% as shown in the figure. The interaction part is evaluated using the standard formalism used by Singh *et al.* [13] with the expression for the Ramakrishnan-Yussouff (RY) functional,

$$\Delta F_{\mathrm{ex}} = -\frac{1}{2}\int d\vec{r}_1\int d\vec{r}_2$$
$$\times\, c(|\vec{r}_1 - \vec{r}_2|;\rho_o)\delta\rho(\vec{r}_1)\,\delta\rho(\vec{r}_2), \quad (6)$$

that gives the difference in the free energies of the solid and liquid phases of average density ρ_o. Here $\delta\rho(\vec{r})$ is the density fluctuation from the average value ρ_o. We use the solution of the Percus Yevick (PY) equation with the Verlet Weiss correction for the direct correlation function, $c(r)$ [18,19]. The low α minimum becomes more stable than the homogeneous liquid state ($\alpha \to 0$) beyond $\eta = 0.576$ ($\rho_o = 1.10$). In order to clarify this point we have shown in Fig. 2, the minimum value for the difference of the free energy per particle (for the corresponding α value) against the density. The corresponding hard sphere glass state becomes more stable with respect to homogeneous liquid state at average density $\eta = 0.597$ [13]. Moreover, the new minimum found in the strongly overlapping region (low α) can be reached continuously from both the liquid state minima and the hard sphere glass state. We also stress here that the expansion (6) for the free energy of the liquid used in the RY approach is a better approximation for the minima observed at low α than in the case of the highly localized structure called the hard sphere glass. In Fig. 3, we show the free energy evaluated with the density function obtained for alpha extending to small values. The minimum appears at $\alpha \approx 18$ for a ρ_o of 1.12. The free energy minimum identified in Ref. [13] also occurs but for a very high value of α and corresponds to highly localized structures referred to as the hard sphere glass. The free energy corresponding to the low α minima is less than that for the hard sphere glass state throughout the density range we have considered, i.e., $\eta \leq 0.60$. However, if the background lattice is taken as a *regular* crystalline one, then the free energy *does not* show any minimum in the small α region unlike the case of an underlying amorphous structure. This indicates an inhomogeneous structure of strongly overlapping Gaussians centered around regular lattice sites is ruled out. Indeed, such uniform structures are never seen in simulations.

This *minimum is seen only for the amorphous structure* which signifies a heterogeneous density distribution. This can be given a more quantitative form in the following way: The α corresponding to the minimum free energy

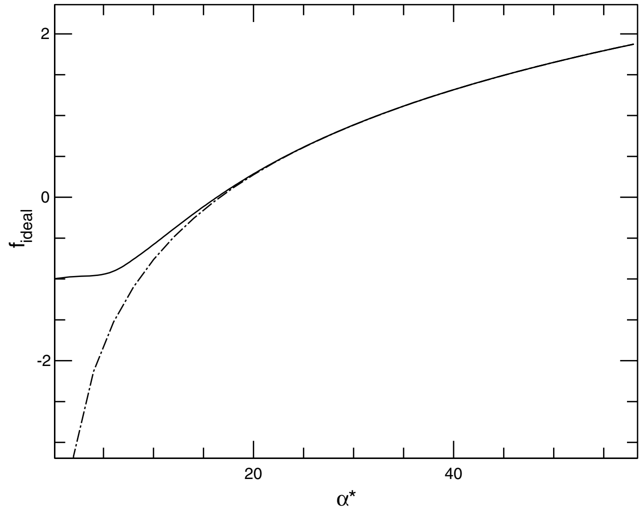

FIG. 1. Ideal gas part of the free energy per particle (in units of β^{-1}) vs α (in units of σ^{-2}) for density $\rho_o^* = 1.0$. The solid line is obtained from the exact evaluation, i.e., Eq. (4), and the dashed line is the result from the approximation.

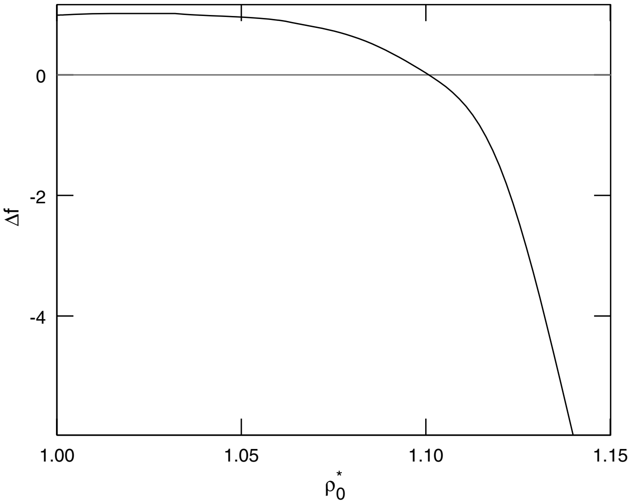

FIG. 2. Free energy difference per particle (Δf) (in units of β^{-1}) vs density in the low α regime.

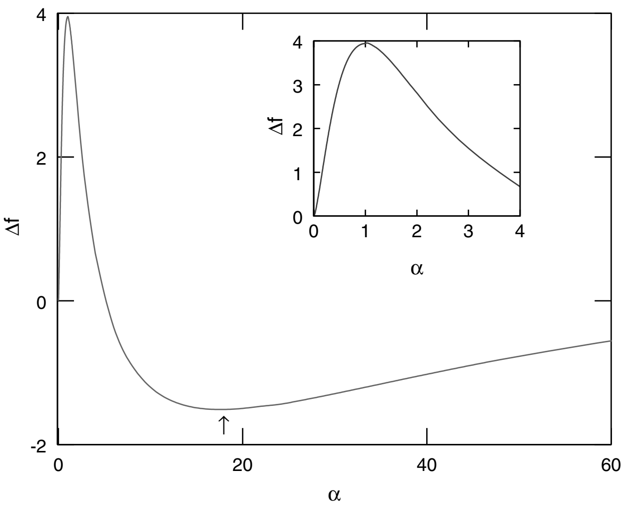

FIG. 3. Difference in free energy per particle (Δf) (in units of β^{-1}) vs α (in units of σ^{-2}) in the low α regime ($\rho_o^* = 1.12$). The inset demonstrates the continuity of the curve near the maximum.

value is inversely proportional to the root mean square displacement of the particles from their sites, which also defines the Lindemann [20] ratio. The two minima with the random structure for low and high value of α, respectively found in the present work and in Refs. [13,15,16] correspond to very different degrees of localization of the particles. The simulation results [5,6] show that the Lindemann ratio of supercooled liquid is approximately 3 times that of crystal at freezing (Fig. 2 of [5]). We have observed a similar relation for the metastable state corresponding to the small α minimum. This is shown in the Fig. 4 where we plot the respective root mean square displacement ($d \sim 1/\sqrt{\alpha}$) for both the supercooled and the crystal case. This fact strengthens the case for identifying it with the supercooled state seen in computer simulations as compared to the highly localized hard sphere glass which shows a level of localization close to that of the corresponding crystal. The barrier height between the homogenous and the heterogeneous phases grows with the increase in the average density, as shown by points in Fig. 5. It follows a power law increase with the height diverging at packing fraction ≈0.62 and exponent 1.57 as shown by the solid line in Fig. 5. In all these calculations we have used $\eta_o = 0.64$. The pressure (P) and Bulk modulus (E) of the corresponding structure are computed using the first and second derivatives of the total free energy per unit volume [16]. We show in Fig. 6 results computed using the present model, for a random structure corresponding to $\eta_o = 0.68$ in (5). The total free energy is calculated using the modified weighted density approximation (MWDA) treatment [11] with a semiempirical form of $c(r)$ [21].

We have also considered the fluctuation of the Gaussian density profile's width parameter α over different sites in the random lattice to incorporate a higher degree of heterogeneity. This is modeled by attaching an independent probability distribution function, $P(\alpha_i)$, *to each lattice site*, that governs α value. We chose P to be Gaussian peaked at $\bar{\alpha}$ and spread (half-width) $\bar{\alpha} r$, to compute the free energy averaged over the α fluctuations as a function of the parameters $\bar{\alpha}$ and r. These fluctuations in α bring about an overall increase in the free energy of the system, i.e., the system stability decreases on account of increased heterogeneity at the individual unit of mass concentration. This is also self-consistent with the choice of using the direct correlation function of a hard sphere system with single size.

The motivation of this study has been to evaluate the stability of heterogeneous density distributions from a purely thermodynamic viewpoint. The existence of the free energy minimum corresponding to a density distribution

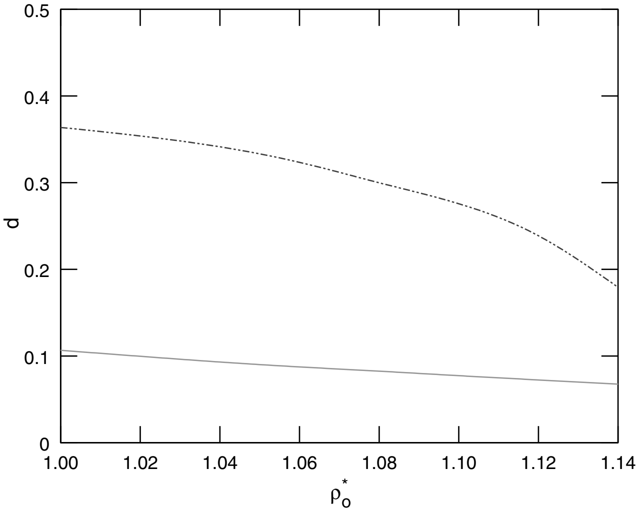

FIG. 4. Average displacement d (in units of σ) vs ρ_o^*. The dashed curve depicts the supercooled phase and the solid line is for the fcc crystal.

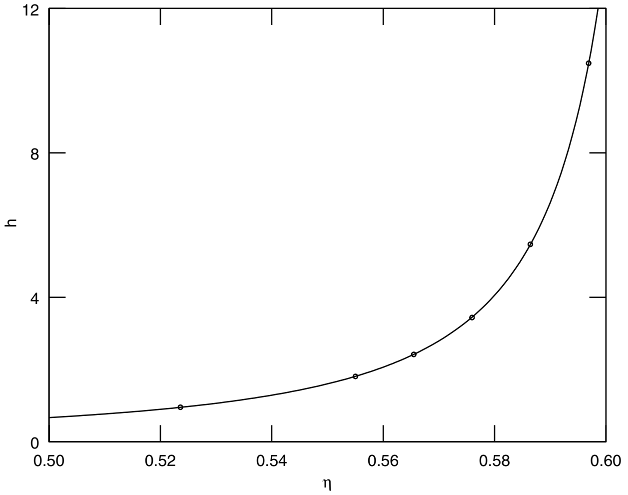

FIG. 5. Barrier height h (in units of β^{-1}) between the liquid and the supercooled phase vs the average packing fraction η. The solid line is a power law fit to these data.

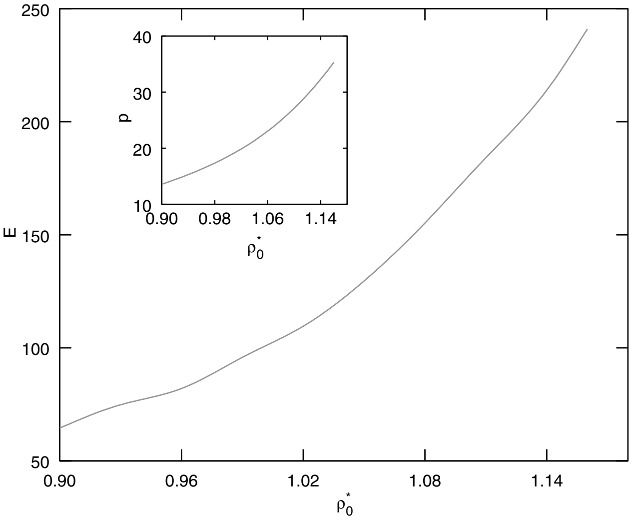

FIG. 6. The bulk modulus E [in units of $(\beta\sigma^3)^{-1}$] vs density for the amorphous structure. In the inset, pressure P [in units of $(\beta\sigma^3)^{-1}$] vs density is shown.

of overlapping Gaussians centered around an amorphous lattice depicts the deeply supercooled state with a heterogeneous density profile. This state can be reached continuously from the homogeneous liquid state or the so-called hard sphere glass minimum. As the density increases, the energy barrier to come out of this minimum grows. The identification of this inhomogeneous state is indeed linked to the proper evaluation of the ideal gas part of the free energy. In earlier works this was generally approximated by the asymptotic formula given in Eq. (3) which works well for large values of α representing highly localized structures. In the present work with the proper evaluation of the ideal gas term for the heterogeneous density, the role of configurational packings on the free energy is taken into account. From our comparison with the Lindemann parameter values (Fig. 4) it follows that this heterogeneous state with a lesser degree of mass localization does agree with the computer simulation results better, as compared to the so-called hard sphere glass observed by Singh *et al.* [13]. This new minimum does not occur for the structure centered on an ordered lattice like the fcc strengthens the case for the heterogeneous glassy phase.

The qualitative nature of this state is different from the hard sphere glass state. The eventual transition of the liquid into any of these states will be determined by considering the dynamics of fluctuations around these minima. The present work is intended to explore the nature of the free energy landscape in the deeply supercooled state. The transformation between different minima will depend on the smearing effects due to coupling of fluctuations. We have used here the Bernal packing to define the underlying lattice, but these studies can be extended to different types of random structure, even taking results from computer simulation studies. We also mention that this new minimum shows up for different forms of the density-functional theory and with different direct correlation functions. This minima is observed with the treatments of both the RY functional and the MWDA [11] even with the PY $c(r)$ without any tail. Indeed, improvement of these results can be obtained with a better input for the structure functions using improved techniques [22]. Including higher order correlations, namely the three point functions, in the expression (6) is also expected to account for increased cooperativity at high density.

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