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Characteristic temperatures of glassy behaviour in a simple liquid

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Abstract

A model for the metastable liquid in terms of holes present in the amorphous structure is considered using the classical density functional theory (DFT). For a one component Lennard-Jones liquid we obtain the temperature dependence of the free volume v_f in the metastable state. A temperature T_0 , similar to that of the characteristic transition of the free volume theory, is identified by extrapolating $v_f(T)$ to zero. The Kauzmann temperature T_K is also obtained here by extrapolating the entropy difference between the supercooled state and that of the crystal to zero. We compare the temperatures T_0 and T_K obtained in our model with other two characteristic temperatures for glassy behaviour, namely (a) the dynamic transition temperature T_c of the mode coupling theory (MCT) and (b) the glass transition temperature T_g which was obtained by Leonardo *et al* (2000 *Phys. Rev. Lett.* **84** 6054) from studying the violation of the fluctuation–dissipation theorem. All the four temperatures, obtained from independent routes, are located with respect to the melting temperature T_m in a manner which is in agreement with experiments.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The physics of a supercooled liquid approaching vitrification is marked by various characteristic temperatures. The transition of the isotropic liquid into a crystalline state with long range order occurs at the freezing point T_m . However, most liquids can be supercooled below the freezing point, bypassing crystallization. The undercooled state is amorphous and is metastable between the liquid and the crystal. The viscosity of the liquid keeps increasing with supercooling and when it reaches a value $\sim 10^{14}P$ the relaxation time becomes comparable to the laboratory timescale, implying that the observed liquid is in an out of equilibrium state. The temperature at which this happens depends on the cooling rate of the liquid, and its value in the zero cooling rate limit is referred to as T_g , the calorimetric glass transition temperature [1]. Another temperature T_0 is associated with glasses by fitting the relaxation time τ with the

empirical Vogel–Fulcher form $\tau \sim \exp[A/(T - T_0)]$, such that τ tend to diverge at $T \rightarrow T_0$. In general, the temperature T_0 is found to be lower than the calorimetric transition temperature T_g . Another temperature T_c of the mode coupling theory (MCT) [2] is identified with glassy behaviour in the temperature range higher than T_g but lower than the freezing point T_m . The MCT, which takes into account the effects of strongly correlated dynamics of the dense liquid, predicts a dynamic transition in the liquid at T_c . Although this occurs only in an idealized version of the MCT, it is now experimentally established that the supercooled liquid undergoes a dynamic crossover around T_c . Finally, there is the Kauzmann temperature T_K which refers to a limiting point below which the extrapolated entropy of the disordered liquid state would become less than that of the ordered crystal [3].

The several temperatures listed above are related either to the thermodynamic properties, or to the dynamic behaviour of the liquid. Both of the above two aspects are crucial in our understanding of the physics of glassy systems. In this paper we present a simple statistical mechanical model for the supercooled liquid using classical density functional theory (DFT). This is motivated to capture the strongly heterogeneous nature of the metastable liquid. Using the structure of the corresponding homogeneous liquid as the only input in the model, we obtain here three of the above referred characteristic temperatures, namely T_0 , T_K , and T_c . This is also compared to T_g obtained in recent studies on the possible violation of the fluctuation–dissipation theorem (FDT) in the same system. The relative locations of the different temperatures as computed in the present work (all in the supercooled region below T_m) are consistent with the corresponding experimental results for a typical glass forming system.

We adopt here a density functional approach [4, 5] for computing the properties of the amorphous state. The key thermodynamic property of the metastable state we focus on is the free energy F , treated as a functional of the inhomogeneous density function $\rho(\mathbf{r})$. For the glassy structure the construction of the density function is guided by the methods adopted for constructing the same quantity in the DFT for the crystalline state. In the crystal $\rho(\mathbf{r})$ is represented as a sum of localized density profiles centred around the sites on a regular lattice with long range order. In the amorphous state the particles are less localized. Note that the word localization is used somewhat loosely in the present context and is applicable only over initial timescales. The mean square displacement of a tagged particle in the amorphous state reaches a plateau over such timescales and is larger than that in a crystal. However, the long time diffusion coefficient is always finite in the supercooled liquid unlike that in the perfect crystal. Furthermore, the idea of an underlying (amorphous) lattice is used here for defining the inhomogeneous density function referred to a timescale over which the atoms vibrate about their mean positions. Such metastable structures correspond to the local minima of free energy [6, 7]. In fact for the dense amorphous state, it is observed that some particles are more mobile than the others [8–11]. Generally in models for glassy behaviour, a timescale for ergodicity restoration in the supercooled state is always involved either directly or otherwise. Hence all discussions of particle localization and the random lattice in the present context are only valid over such timescales.

The occurrence of the voids in a dense structure is the central idea used in the free volume [12, 13] model of glass transition. The possibility of having voids in a dense structure has important implications for its transport properties. Here the concepts of liquid-like and solid-like clusters were introduced from a phenomenological picture of the supercooled liquid and percolation theory was used to predict that at some critical density the transport process gets completely frozen, giving rise to very long relaxation times. The disappearance of the minimum free volume needed for the mass transport is crucial in the jamming of the system. In the present work we consider the metastable liquid as a heterogeneous structure with an accumulation of holes. The stability of an amorphous structure is tested relative to that of the

crystalline or the uniform liquid state. Using the number of voids in the system corresponding to the optimum free energy we define the free volume at that state, and by extrapolating the temperature dependence of this free volume to zero we obtain the temperature T_0 . This is similar to the transition obtained in the free volume picture. The Kauzmann temperature T_K is computed by calculating the entropy of the amorphous metastable state and comparing it to the corresponding crystal state entropy.

We organize the paper as follows. In the next two sections we present the density functional model studied and outline the computation of T_0 and T_K respectively. Following this in section 4 we indicate how our results can be viewed in the light of information obtained from other models. In this respect we discuss the temperatures T_c and T_g for the same one component Lennard-Jones system. We end the paper with a discussion of the results in section 5.

2. The model studied

2.1. Inhomogeneous density function

An important step in the construction of the density functional model for the supercooled state is the proper parametrization of the inhomogeneous density function $\rho(\mathbf{r})$. We follow closely the methodology adopted for the DFT of the crystalline state. However, the present case is unlike that of the crystal in which $\rho(\mathbf{r})$ satisfies the basic symmetry of the crystal structure. The ensemble averaged density is expressed here as a collection of strongly overlapping Gaussian profiles [14] centred over a set of lattice sites $\{\mathbf{R}_i\}$ which are distributed randomly [6, 15, 16].

$$\rho(\mathbf{r}) \equiv \sum_i \phi_\alpha(\mathbf{r} - \mathbf{R}_i) = \sum_i (\alpha/\pi)^{3/2} \exp(-\alpha(\mathbf{r} - \mathbf{R}_i)^2). \quad (1)$$

The width of Gaussian profiles is inversely proportional to the square root of α , which from here on will be referred to as the width parameter. For the amorphous structure it is expected to be broader than that for the crystal, and represents the higher mean square displacement of a particle about its mean position. Strictly speaking, for the strongly heterogeneous structures the width parameters at the different sites of the amorphous lattice should be considered to be different. However, we will approximate them to be the same here for simplicity. In this representation, the limit $\alpha \rightarrow 0$ is the homogeneous liquid state and higher values of α represent increasingly localized structures. To account for the presence of voids in the structure, the parameter space of the density function $\rho(\mathbf{r})$ is extended by considering an underlying structure $\{\mathbf{R}_i\}$ in which a fraction of the sites do not include a Gaussian profile. Let N_p be the number of lattice sites in volume V out of which N sites are occupied by the particles. N_D sites in the lattice are unoccupied, presenting the same number of holes randomly distributed ($N_p = N + N_D$). The density function for the structure with voids is now represented as $\tilde{\rho}(\mathbf{r}) = \sum_{i=1}^{N_p} \sigma_i \phi_\alpha(\mathbf{r} - \mathbf{R}_i)$, where σ_i takes the value 1 or 0, depending on whether the site at \mathbf{R}_i is occupied or empty, the distribution of $\{\sigma_i\}$ being statistically independent of that of \mathbf{R}_i . The density function averaged over all positions of the vacancies is obtained as

$$\rho(\mathbf{r}) = \mathcal{A} \sum_{i=1}^{N_p} \phi_\alpha(\mathbf{r} - \mathbf{R}_i), \quad (2)$$

where $\mathcal{A} = N/N_p$ is the average occupation of the site. We assume the void sites or the holes to be distributed homogeneously throughout the system and hence this fraction is the same for all the shells around any arbitrary position in the lattice. This results in a corresponding decrease in the number of occupied sites in each co-ordination shell around any arbitrary point in the system. This test density function which we will be using in our DFT model for studying the thermodynamic properties of the metastable state is characterized by the following three quantities:

- (a) The width parameter α : in the search for the free energy minima which is appropriate for the heterogeneous state with voids we restrict ourselves to α values much smaller than those typical for a crystal.
- (b) The occupation fraction \mathcal{A} : for representing voids in the structure we focus on the case $\mathcal{A} < 1$.
- (c) A set of lattice points \mathbf{R}_i distributed on the fixed random structure. In the present calculation the amorphous lattice is represented in terms of the Bernal packing. This is further illustrated below.

2.2. Free energy

In order to obtain the inhomogeneous density for the equilibrium state we apply the thermodynamic extremum principle for the suitable free energy functional. Instead of considering the coexistence of the two phases at constant pressure, we focus here on the canonical ensemble (constant N, V, T) for the single phase and minimize the Helmholtz free energy for the system. The number of holes in the supercooled state changes by an optimum arrangement of the particles by varying N_p . For the crystalline state this would imply adjusting the lattice constant so that the vacancy concentration can change in the fixed volume with the same number of particles. In the amorphous case this implies a somewhat less restrictive situation of finding the optimum number of holes in the given volume with a fixed number of particles. The variational parameter corresponding to N_D in the density function is \mathcal{A} . The total free energy is computed as a sum of two parts, the ideal gas term and the interaction term, $F[\rho] = F^{\text{id}}[\rho] + F^{\text{ex}}[\rho]$. The ideal gas term of the free energy functional (in units of the Boltzmann factor $k_B T = \beta^{-1}$) is given by

$$F^{\text{id}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) (\ln[\wedge^3 \rho(\mathbf{r})] - 1) \quad (3)$$

\wedge being the thermal wavelength [17] appearing due to the momentum variable integration in the partition function. The RHS of equation (3) is a simple generalization of the ideal gas part of the free energy for the nonuniform density, i.e. $\rho \rightarrow \rho(\mathbf{r})$ [18]. The interaction ΔF^{ex} part (excess over the value for the uniform liquid state) is evaluated using the standard expression for the Ramakrishnan–Yussouff (RY) functional [19] involving a functional Taylor series expansion in terms of the density fluctuation $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0$ around the liquid phase of average density ρ_0 [19, 20],

$$\Delta F^{\text{ex}} = -\frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 c(|\mathbf{r}_1 - \mathbf{r}_2|; \rho_0) \delta\rho(\mathbf{r}_1) \delta\rho(\mathbf{r}_2) \quad (4)$$

where $c(r; \rho_0)$ is the Ornstein–Zernike direct correlation function [17] of the corresponding homogeneous liquid state. From here on we drop explicitly mentioning the dependence of $c(r)$ on the thermodynamic parameters like density ρ_0 and temperature T to keep notations simple. Using (1) in (4), we express the product terms (which arise from the product of $\rho(\mathbf{r})$ at two different points in space) involving the summation over the double indices i and j into a self part ($i = j$) and an interaction part ($i \neq j$). The excess free energy difference ΔF^{ex} between the heterogeneous state and the uniform liquid is finally approximated as

$$\begin{aligned} \Delta F^{\text{ex}}[\rho(\mathbf{r})] &= \frac{N\rho_0}{2} \int d\mathbf{r} c(r) - \frac{1}{2} \sum_{i=1}^{N_p} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_\alpha(\mathbf{r}_1 - \mathbf{R}_i) \phi_\alpha(\mathbf{r}_2 - \mathbf{R}_i) c(r_{12}) \\ &\quad - \frac{1}{2} \sum'_{i,j=1}^{N_p} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_\alpha(\mathbf{r}_1 - \mathbf{R}_i) \phi_\alpha(\mathbf{r}_2 - \mathbf{R}_j) c(r_{12}), \end{aligned} \quad (5)$$

with $|\mathbf{r}_1 - \mathbf{r}_2| = r_{12}$. The prime in the third term on the RHS of (5) implies that $i \neq j$ and the pairwise sum is evaluated in terms of the site to site correlation function $g_A(R)$ for the amorphous structure. The sum over the index j for a fixed i appearing in this term is evaluated by adding contributions from concentric shells with common origin at the i th site. Adding the contributions from these shells we obtain an integral over the radial vector R . In this integral, at a given radius R , the number of occupied sites (each centring a Gaussian profile) in the corresponding shell is taken as a weight factor. The number of such sites within a shell of radii R and $R + dR$ is counted as $4\rho_0\pi R^2 g_A(R) dR$. In a similar way the second term in the RHS of (5) also reduces to an integral over R , but now weighted by $\delta(R)$ to include only the $i = j$ case. The total free energy is computed by adding the different contributions coming from the origin being placed at site i for $i = 1-N$. For the isotropic system each of these N contributions are assumed to be the same. Hence combining the second and the third term together we obtain for the excess free energy per particle

$$\Delta f^{\text{ex}} = \frac{\rho_0}{2} \int d\mathbf{r} c(r) - \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{R} \phi_\alpha(\mathbf{r}_1) \phi_\alpha(\mathbf{r}_2 - \mathbf{R}) c(r_{12}) (\mathcal{A}\delta(\mathbf{R}) + \rho_0 g_A(R)). \quad (6)$$

In an exactly similar way using density function (1), the contribution to ΔF per particle from the ideal gas part (given by (3)) is obtained as

$$f^{\text{id}} = \int d\mathbf{r} \phi_\alpha(\mathbf{r}) \left[\ln \left(\int d\mathbf{R} \phi_\alpha(\mathbf{r} - \mathbf{R}) (\mathcal{A}\delta(\mathbf{R}) + \rho_0 g_A(R)) \right) - 1 \right]. \quad (7)$$

The two expressions (7) and (6) will be the starting point of evaluating the free energy corresponding to the inhomogeneous density function defined in terms of the parameters α and \mathcal{A} and the underlying amorphous structure represented in terms of the pair function g_A .

3. Results

For the one component Lennard-Jones (LJ) system the density and temperature are expressed in standard LJ units of σ^{-3} and ϵ/k_B respectively. The dependence on these thermodynamic parameters enters the model in terms of that of the direct correlation function $c(r)$ of the homogeneous liquid state. $c(r)$ at a given density and temperature is obtained using standard results of liquid state theory. In doing this we are in fact extending the theories of the normal liquid in the supercooled domain. For the Lennard-Jones liquid at the high densities studied here, we use the bridge function [21] method solution for the structure factor. This gives distinct advantages over choosing the hard sphere system [22] since we are able to study the temperature dependence of the free volume instead of having only the density as the relevant variable. The total free energy is minimized with respect to the width parameter α and the fraction $\Delta = (1 - \mathcal{A})$ of holes. This is shown in figure 1 for the chosen density $\rho_0 = 1.04$ and temperature $T = 0.8$. The corresponding direct correlation function $c(r)$ which is used for computing the free energy is shown in figure 2. Apart from the direct correlation function $c(r)$ the only other input for the present model is the random structure $\{\mathbf{R}_i\}$ underlying the heterogeneous density distribution of overlapping Gaussian profiles. This amorphous lattice is obtained in terms of a site-site correlation function $g_A(R)$ for which we have used the Bernal's random structure [23] of a hard sphere system generated through the Bennett's algorithm [24]. We make the approximation $g_A(R) \equiv g_B[R(\eta/\eta_0)^{1/3}]$, where the g_B refers to the pair correlation for the Bernal's structure. $\eta = \pi\rho_0 d^3/6$ denotes the average packing fraction for the equivalent hard core system of diameter d [17] corresponding to the one component Lennard-Jones system studied here. The quantity η_0 is used as a scaling parameter

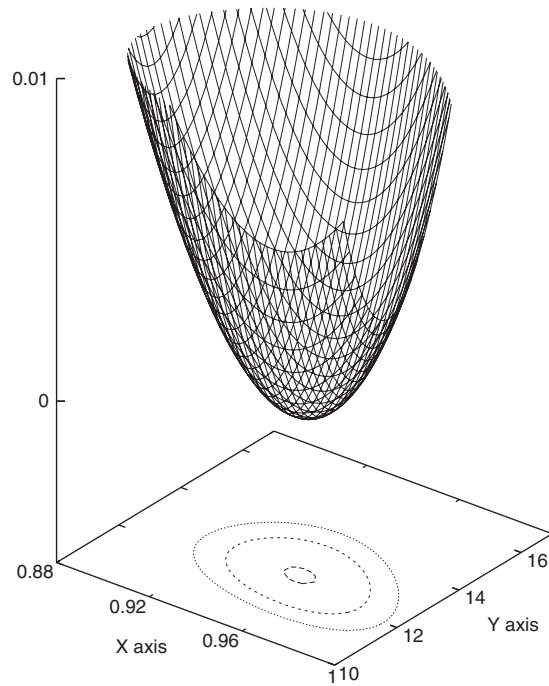


Figure 1. The free energy per particle f on the parameter space of A (X axis) and $\alpha\sigma^2$ (Y axis) at $\rho_0 = 1.04$ and $T = 0.8$. f is expressed in units of $k_B T$ and its value at the minimum is chosen to be zero. The contours of constant f are shown on the A - α plane.

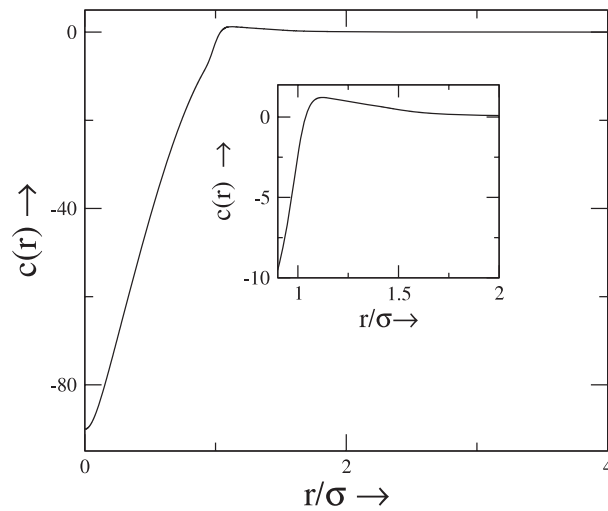


Figure 2. Direct correlation function $c(r)$ versus r/σ at density $\rho_0 = 1.04$ and temperature $T = 0.8$ obtained from the bridge function method [21]. The behaviour of $c(r)$ near the minimum of the Lennard-Jones potential well is magnified in the inset.

for the structure [25], such that at $\eta = \eta_0$ the pair correlation $g_B(R)$ for the Bernal's structure is obtained. The Bernal's structure at close packing is shown in figure 3. We have followed here the conventional choice [26] that $g_B(R) = 0$ for $\sigma < R < 1.025\sigma$. The calculation of the

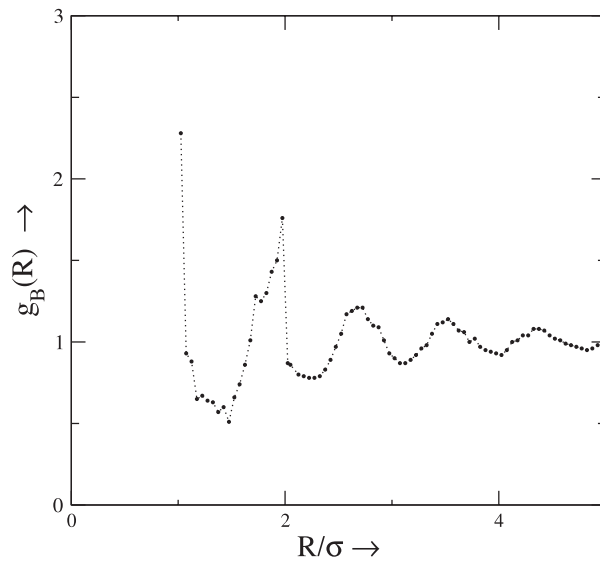


Figure 3. Site to site correlation function $g_B(R)$ versus R/σ obtained in the Bennets algorithm at closed packing [24].

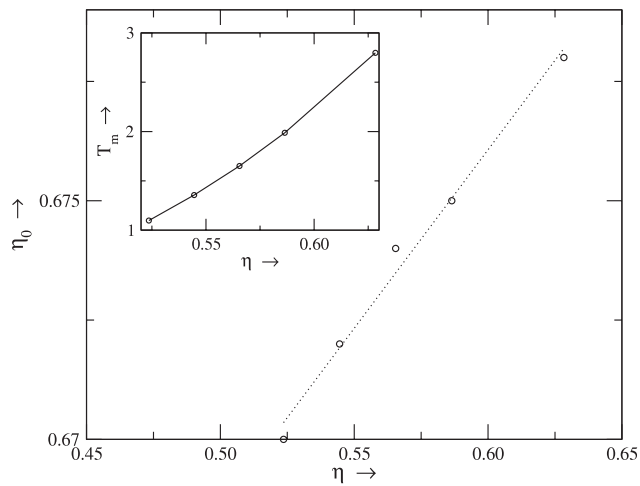


Figure 4. Variation of the parameter η_0 (see text) with the corresponding packing fraction η to characterize the aperiodic structures used for identifying the metastable amorphous states below freezing temperature T_m . The inset shows the variation of the corresponding melting temperature T_m with respect to η .

free energies shows that the amorphous structure become metastable between the liquid and the crystal state at high densities. In presenting our results here, we choose the parameter η_0 for $g_A(R)$ such that at a given density ρ_0 the heterogeneous state becomes metastable between the homogeneous liquid and the crystal once the temperature goes below the corresponding freezing temperature T_m . For $\rho_0 = 1.0$, using the g_B at $\eta_0 = 0.67$ we obtain the free energy of the amorphous state less than that of the uniform liquid state below $T < 1.10$ which is the value of T_m at the density $\rho_0 = 1.0$. In figure 4 we show the variation of the optimum η_0 with the corresponding density ρ_0 . The T_m values at the same ρ_0 values are shown in the inset.

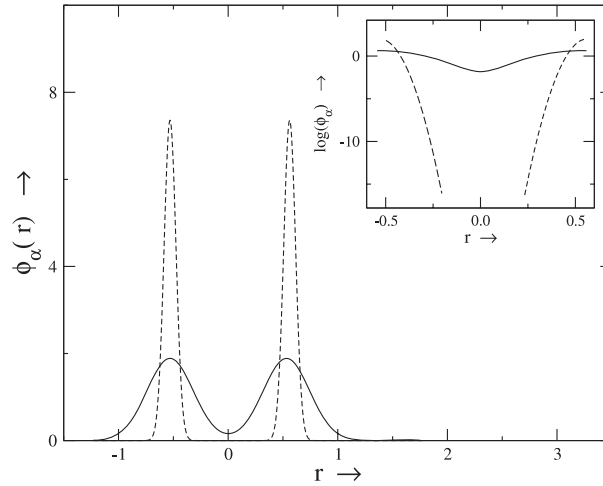


Figure 5. Comparison (schematic, in one dimension) between the Gaussian profile of the amorphous structure and that of the crystal, at $\rho_0 = 1.0$ and $T = 0.8$. Width parameters (α) for the two displayed Gaussian profiles are set equal to the optimum values at the respective free energy minima. The inset shows the strong overlapping nature of the density profiles in the amorphous case as compared to that in the crystal. The Y axis in the inset is shown in the logarithmic scale for better magnification.

From the minimization of the free energy it turns out that the optimum value of the width parameter α at the free energy minimum for the amorphous structure *is smaller* than the typical α value at the minimum corresponding to a crystalline structure. This shows that the extended density distribution scenario presented above for the supercooled metastable state is self-consistent. For the small α values the F^{id} needs to be evaluated numerically [6]. The metastable free energy minimum obtained, corresponding to the amorphous structures with overlapping density profiles, has proven to be robust to the variation of different types of interaction potentials and the input direct correlation function $c(r)$ for large r [15] in equation (4). Using the results from the present model we can judge the importance of including the presence of holes in the amorphous structure. If the holes are assumed to be absent, i.e. for $\mathcal{A} = 1$, the free energy at the minimum (now minimized with respect to the width parameter α only) *is higher than* the corresponding optimum free energy obtained in the present calculation. The presence of voids in the structure is therefore more favourable energetically. In order to demonstrate the more overlapping nature of the density profiles in the amorphous structure as compared to that in the crystal, we have shown in figure 5 the corresponding Gaussian profiles (in one dimension). The respective α values correspond to the free energy minimum representing the amorphous or the crystalline states. The separations of the Gaussian centres are chosen to be respectively equal to the position of the first peak in $g_A(R)$ for the amorphous state and the lattice constant for the crystalline state.

We assume that the void sites considered in the model constitute around each of them a hole of radius $R_h \sim 1/\sqrt{\alpha}$, where α is the Gaussian width parameter corresponding to the optimum free energy. Accordingly R_h changes with temperature and becomes smaller with lowering of the temperature as shown in figure 6. Experimentally, the size of voids in an amorphous structure can be obtained from positron annihilation lifetime spectroscopy (PALS). The average size of the holes found in such studies shows a similar decreasing trend with temperature as displayed for R_h in our theoretical model. The experimental data from two

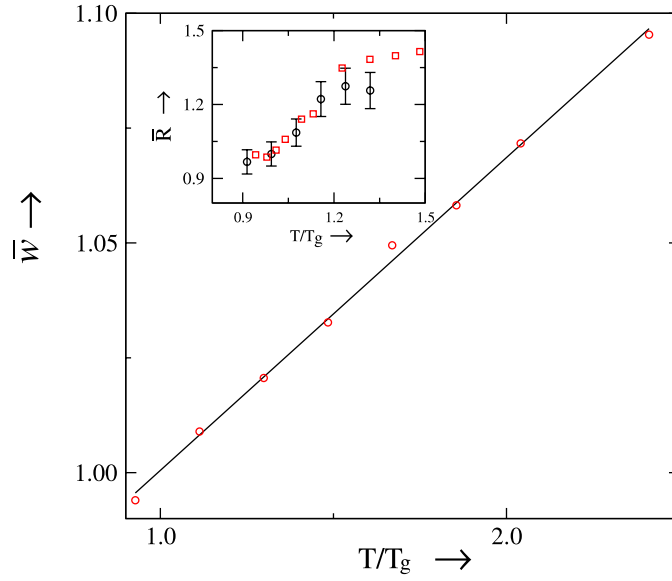


Figure 6. The relative width \bar{w} of the Gaussian profiles (i.e., ratio of $1/\sqrt{\alpha}$ with the corresponding value at $T = T_g$) versus T/T_g at density $\rho_0 = 1.04$. T_g is obtained from [36]. The inset shows the experimental data for OTP [28] (circle), [27] (square) for the average size of the holes (scaled w.r.t. its value at $T = T_g$ for OTP) versus T/T_g .

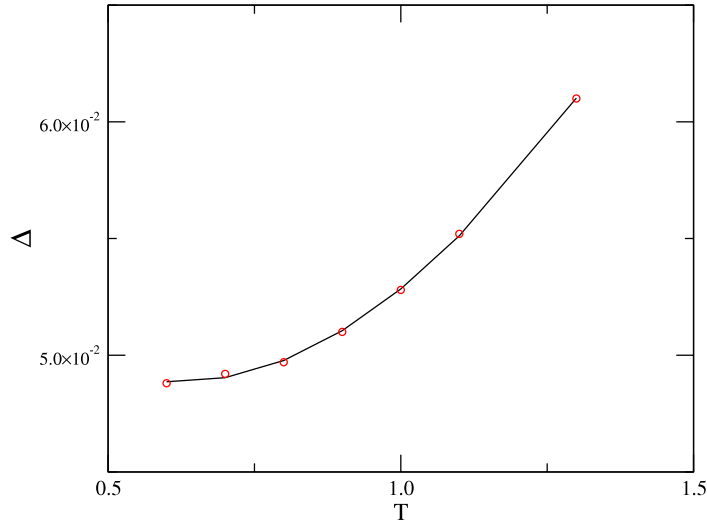


Figure 7. Variation of vacant sites Δ versus temperature T (in units of ϵ/k_B) at density $\rho_0 = 1.04$.

different studies, both with a typical glass forming system OTP [27, 28], are shown in the inset of figure 6. In our model the corresponding fraction Δ of the number of holes decreases with temperature. The variation of the optimum value of Δ corresponding to the free energy minimum with temperature T at constant density $\rho_0 = 1.04$ is shown in figure 7. The ratio v_h of the void associated with the holes (total no of such holes = ΔN_p) to the total volume V of the system is obtained as $v_h = (4/3)\pi\rho_0(\mathcal{A}^{-1} - 1)\alpha^{-3/2}$. We count the spherical holes of radius

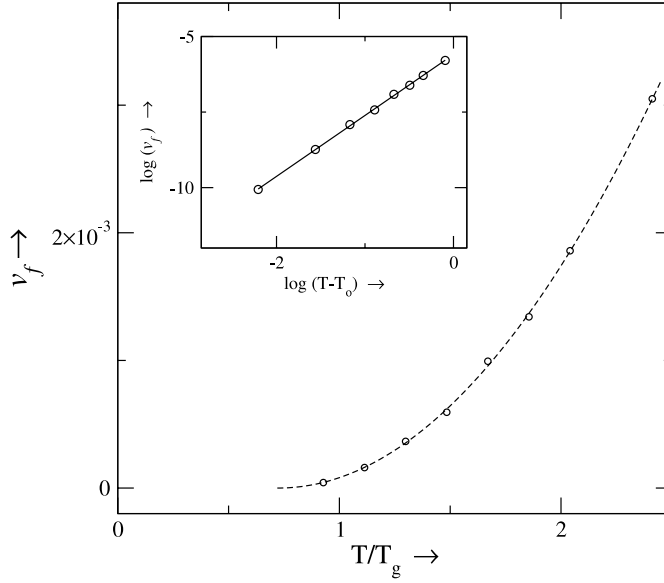


Figure 8. Variation of the relative free volume v_f (see text) with T/T_g ; the dashed line is the fitted curve in v_f which is going to zero at T_0/T_g . The inset shows the variation of v_f and $T - T_0$ in the logarithmic scale at density $\rho_0 = 1.04$.

R_h centred on the sites which are vacant. The amount of void v_h approaches a plateau with decrease of temperature T . This behaviour is demonstrated in figure 8 for constant density $\rho_0 = 1.04$. If we assume that the excess of v_h above the plateau value v_0 (say) is what is available for particle movement, a complete jamming or localization of the particles occurs when $v_h \rightarrow v_0$. The excess volume v_f such that $v_h = v_0 + v_f$ is defined to be the free volume. A characteristic temperature is identified from the behaviour $v_f \rightarrow 0$ as $T \rightarrow T_0$. We obtain T_0 in our model by fitting v_h to the form $v_h = v_0 + A(T - T_0)^2$, as shown in figure 8. A similar behaviour of the temperature dependence of the free volume was reported recently for a polymeric system [29] with an exponent 1.46 ± 0.07 .

In the thermodynamic approach to understanding the glass transition, the idea of distribution of free volume [12, 13] in the dense liquid has been used. There it is assumed that the accumulation of free or excess volume is crucial for mass transport in the liquid. Thus the temperature T_0 at which the amount $v_f \rightarrow 0$ is analogous to the free volume transition temperature [13]. The volume v_0 is the relative amount of the void in the glassy phase and it decreases with the increase of liquid density. In figure 9, we plot the saturation value of v_0 versus the corresponding density ρ_0 . As the liquid becomes more dense the corresponding low temperature limit of the void also becomes less due to increased compactness. This is plausible in the context of the present model. It is useful to note also that in our calculation the free volume approaches zero as $T \rightarrow T_0$. This implies that the relaxation time should diverge at this temperature according to the conventional link assumed between the free volume and glassy relaxation through the Doolittle hypothesis [12, 30]. T_0 is similar to the Vogel–Fulcher temperature though it is not possible to ensure here that they are identical.

The supercooled state of the liquid is also characterized by the Kauzmann temperature T_K [3]. Since we are calculating the thermodynamic properties of the metastable state in our present DFT model for the Lennard-Jones system, we are able to calculate the entropy of the

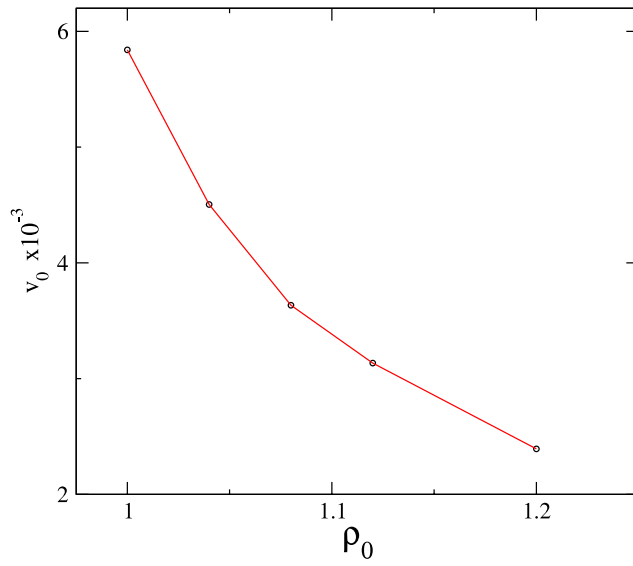


Figure 9. Variation of the saturated volume i.e. v_0 (as a fraction of the total volume) with respect to the density ρ_0 (in units of σ^{-3}).

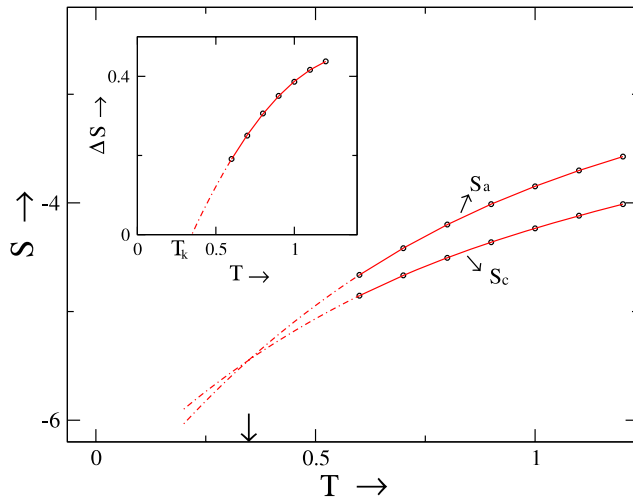


Figure 10. The variation of the crystal state entropy S_c (in units of k_B) and amorphous state entropy S_a w.r.t. temperature T (in LJ units of ϵ/k_B) at $\rho_0 = 1.04$. The inset shows the difference $\Delta S = S_a - S_c$ going to zero at T_K .

metastable state as well. The free energy in the supercooled state is obtained as a function of temperature and from this we compute the entropy $S = -(\partial F/\partial T)_V$. In the present case using the Ramakrishnan–Yussouff approach we actually compute only the difference of the free energy of the metastable supercooled state from that of the uniform liquid state. Therefore, in order to obtain the entropy of the amorphous state we need an estimate for the entropy of the uniform liquid state. For this we use results from computer simulation [31] on Lennard-Jones systems. In figure 10 we plot the change of entropies of the supercooled liquid and that of the

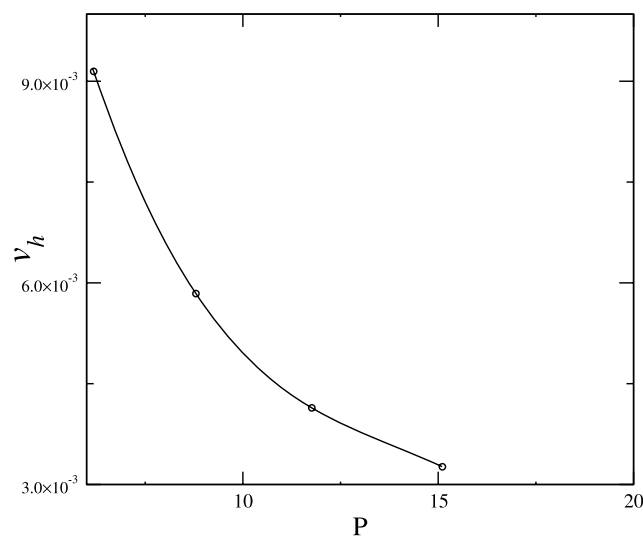


Figure 11. Variation of the excess volume v_h (in units of σ^3) with corresponding pressure P (in units of $k_B T \sigma^{-3}$) at constant temperature $T = 1.0$ (in units of ϵ/k_B).

crystal with temperature at constant density $\rho_0 = 1.04$. The data presented in this figure for the crystal state entropies are computed from the free energy values also obtained in computer simulations [32]. The difference between the entropies of the crystalline and the amorphous state is extrapolated to zero to estimate the Kauzmann temperature T_K . This extrapolated temperature presents a limiting situation since the supercooled liquid cannot remain in the liquid state below $T < T_K$. In that case the entropy of the disordered liquid state (S_a) would be less than that (S_c) of the crystal. It is useful to note here that the free energy of the liquid is computed for the aperiodic structures, which are all characterized in terms of the given pair correlation function $g_A(R)$. This only corresponds to one set from the multitude of possibilities (inherent structures [33]). Our computation of the free energy and hence the entropy is also restricted by this choice of a specified set of structures.

Pressure dependence of the relaxation behaviour of a glass forming liquids has been of much current research interest [34, 35]. We have not focused here on studying how the coexistence of the different phases changes with pressure. However, it is possible to obtain an estimate for the equilibrium pressure from the free energy of the metastable state. In figure 11 we show the dependence of the pressure in the supercooled liquid (obtained using the relation $P = -(\partial F/\partial V)_T$) on the corresponding free volume fraction v_h . With increase of pressure P , the free volume v_h decreases, indicating more compactness in the structure.

4. Relation to other models

In the previous section we have obtained the values for the Kauzmann temperature T_K as well as the temperature T_0 at which the free volume tends to zero. In the present section we consider the estimates for two more characteristic temperatures in the supercooled region for the same Lennard-Jones system. This is done here to test the consistency of our model with other studies on glassy behaviour. In particular, we consider the vitrification or glass transition point T_g , and the mode coupling dynamic transition point T_c . Before discussing those quantities, it is useful to note that all these temperatures in the supercooled region should lie below the

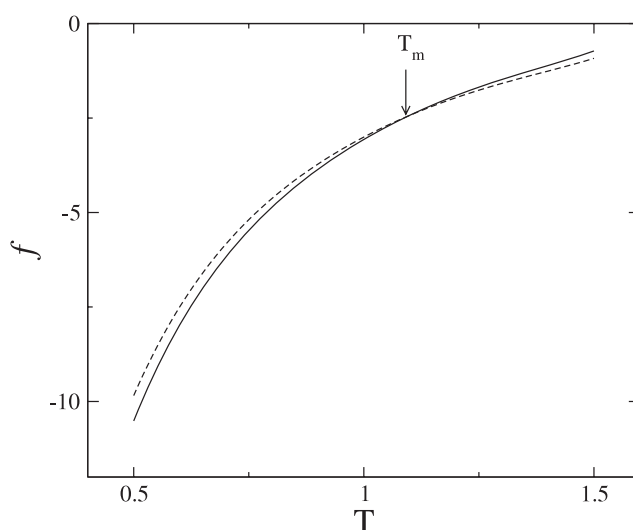


Figure 12. Free energy (in units of $k_B T$) of the liquid state (dashed line) and fcc crystal (from solid line) versus T (in units of ϵ/k_B) for the Lennard-Jones system. Crossover of the free energy shows the freezing point $T_m = 1.10$ of the LJ system at constant density $\rho_0 \sigma^3 = 1.00$.

freezing point at which the liquid undergoes a thermodynamic transition to a crystalline state. The thermodynamic state of the many particle system at a given temperature is the one with lowest free energy. Therefore, in order to obtain T_m , we compare the free energies of the crystalline state and the uniform liquid state. In figure 12 we display the free energy curves for the Lennard-Jones system in the homogeneous liquid and solid states for the constant density $\rho_0 = 1.0$ showing a cross-over from the liquid to the crystalline state at $T_m = 1.10$. The results for the free energies of the liquid and crystal, as displayed in figure 12, are obtained from computer simulation data of [31] and [32] respectively.

4.1. The glass transition temperature T_g

Since one component Lennard-Jones systems tend to crystallize quickly it has particularly been difficult to supercool them. However, recently Di'Leonardo *et al* [36] used some special techniques by including a many body term in the interaction potential to avoid crystallization in the one component system and identified a temperature similar to T_g for the system. Here the off-equilibrium dynamics of the monatomic LJ system has been analysed to study the generalized fluctuation-dissipation theorem (FDT) [37]. In equilibrium, the FDT is satisfied and therefore its violation signals that the liquid is falling out of equilibrium. A detailed analysis of the correlation and response functions demonstrated that below a characteristic temperature the FDT for the system modifies to a form corresponding to the one step replica symmetry breaking (1RSB) state [38] proposed in the spin glass theory. This is also shown to be close to the temperature at which the equilibrium potential energy V of the liquid crosses over from the high temperature form $\sim T^{3/5}$ [39] to the harmonic form ($\sim T$). T_g is thus the temperature at which the supercooled liquid develops solid-like properties and is naturally identified with the calorimetric glass transition temperature. The data for T_g from the independent study of [36] serve as useful information for comparing the relative locations of the various characteristic temperatures of glassy behaviour in the present context.

4.2. The mode coupling transition at T_c

Finally, we consider the dynamic transition predicted in the mode-coupling theory of glassy dynamics [2]. The time correlation of density fluctuations $\langle \delta\rho(q, t)\delta\rho(-q, 0) \rangle$ acts as an order parameter in this transition. To discuss the mode coupling model, we consider the Laplace transform of the time correlation function (normalized w.r.t. its equal time value) of density fluctuations at wavenumber q as

$$\psi(q, z) = \frac{1}{z - \Omega_q^2 \{z + iq^2 \Gamma^R(q, z)\}^{-1}} \quad (8)$$

where $\Omega_q = q/\sqrt{\beta m S(q)}$ is a microscopic frequency of the liquid state, m is the mass of a liquid particle, and $S(q)$ is the static structure factor of the liquid [17]. $\Gamma^R(q, z)$ is the renormalized longitudinal viscosity. The contributions to the transport coefficient Γ^R from the coupling of the slowly decaying density fluctuations constitute a feedback mechanism for producing slow dynamics. The mode coupling contribution [40] to $\Gamma^R(q, t)$ (in addition to a short time or bare part) at the one loop order is obtained as

$$\Gamma^{\text{mc}}(q, t) = \lambda_0 \int \frac{d\mathbf{k}}{2\pi^3} V(\mathbf{q}, \mathbf{k}) \psi(\mathbf{q} - \mathbf{k}, t) \psi(\mathbf{k}, t) \quad (9)$$

where $\lambda_0 = (2\beta\rho_0 m^4)^{-1}$ and the vertex function $V(\mathbf{q}, \mathbf{k})$ is given by

$$V(\mathbf{q}, \mathbf{k}) = S(k)S(|\mathbf{q} - \mathbf{k}|) \left[\frac{\hat{\mathbf{q}} \cdot \mathbf{k} c(k) + \hat{\mathbf{q}} \cdot (\mathbf{q} - \mathbf{k}) c(|\mathbf{q} - \mathbf{k}|)}{q^2} \right]^2. \quad (10)$$

At low temperatures the feedback effects from the coupling of slowly decaying density fluctuations are strong enough to make the viscosity diverge. Approaching from the ergodic liquid side, this occurs at the transition T_c . The time correlation of density fluctuations freezes beyond this point. The temperature T_c signifies an important cross-over point in the dynamics of the supercooled liquid. The exact location of the dynamic instability in the self-consistent model is obtained by solving the basic equations of MCT [40, 41]. In order to explain this let us assume that in the ideal glassy phase the density correlation function $\psi(q, t)$ develops a non-decaying part f_q in the long time limit, i.e.

$$\psi(q, t \rightarrow \infty) = f_q \quad (11)$$

where f_q signifies the non-ergodicity parameter (NEP). Using (11) and taking the long time limit of (8) the following nonlinear integral equation for f_q is obtained.

$$\frac{f_q}{1 - f_q} = \frac{1}{\Omega_q^2} \Gamma^{\text{mc}}(q, t \rightarrow \infty) \quad (12)$$

where $\Gamma^{\text{mc}}(q, t \rightarrow \infty)$ is expressed in terms of the static correlation functions of the density. Equation (12) can be solved numerically by iteration to obtain a final set of f_q . The fluid is considered to have undergone a transition when all the f_q simultaneously converge on a non-zero set of values. The static structure factor of the liquid is used in solving the integral equations (12) for f_q involving $\Gamma^{\text{mc}}(q, t \rightarrow \infty)$ and it therefore controls the exact location of T_c for a specific system. In numerical solution of the integral equations for f_q we choose the upper cut-off Λ for the wavevector q in the mode coupling integrals such that $\Lambda\sigma = 50$. In figure 13 we have shown the nonergodicity parameter f_q for the whole wavevector range at $\rho = 1.04$ with $T = 0.76$. It is found that contributions coming from wavevectors above the cut-off value do not affect the transition point much. For the present case we iterate these integral equations using the same structure factor corresponding to $c(r)$ used in the DFT model described above. The temperature T_c is computed for several different densities of the liquid.

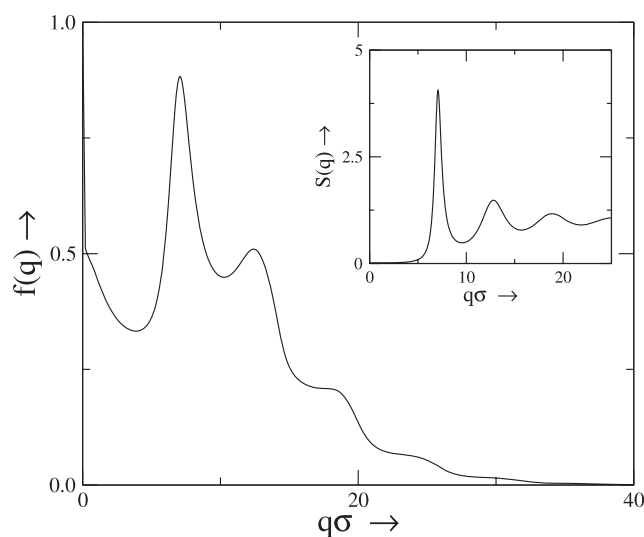


Figure 13. In this figure we have plotted $f(q)$ (non-ergodicity parameter) with $q\sigma$ at transition temperature $T = 0.76$ and at density $\rho_0 = 1.04$. The inset shows the corresponding structure factor $S(q)$ of the LJ system used in the calculation of $f(q)$ at the same density and temperature with q .

5. Discussion

The present model follows from the general approach of describing the glassy state in terms of some kind of defects (analogous to those in the crystalline state) which may be holes [18, 42, 43] or interstitials [44]. The DFT model we present here has been originally applied for computation of concentration of monovacancies in a crystal [45, 46]. We have used the idea of holes in the metastable structure. The crucial ingredient here is the parameterized density function which is identified with the inhomogeneous structure having voids or holes. The holes are assumed to be distributed uniformly in the system and non-interacting. The concentration of holes as obtained from the optimization of the free energy is found to be low, making this basic assumption of the model self-consistent. Using this model we are able to link several characteristic temperatures for the glassy behaviour from a common standpoint.

The definition of free volume in a dense liquid is not unique and is often based on phenomenological grounds for different systems [47, 48]. We adopt a definition for the free volume in an indirect way from the temperature dependence of the void fraction. This is somewhat unusual given the fact that generally the concept of free volume is linked to a more microscopic picture, referring to the single particle motion in a cage formed around a single atom. The computer simulation techniques also investigated the free volume concept adopting a similar microscopic approach [49, 50]. In the original free volume model of Cohen and Grest the idea of liquid-like and solid-like shells (classification depending on the amount of free volume associated with a given atom) was introduced to describe the supercooled state. Based on this a phenomenological expression for the free energy was proposed and analysed to study the nature of the free volume transition. In the present work we have used the density functional approach for computing thermodynamic properties of the amorphous solid-like state, justifying the role of voids in the structure. Invoking the thermodynamic extremum principle we estimated the fraction of the volume that is void. Using the observed dependence of void with respect to temperature we obtain a measure of the free volume (V_f) in the solid. We use only the liquid

structure factor as an input. However, in our theory we estimate the temperature T_0 at which the free volume goes to zero and the Kauzmann temperature T_K only through extrapolation. Thus, unlike the Cohen–Grest theory, the free volume transition is not explicitly proven in the present calculation.

We make the following observations on the present methodology of the density functional calculation.

(A) The density function is expressed in terms of Gaussian profiles centred on a random structure. The width parameter (α) of the Gaussian plays a crucial role in the characterization of the supercooled states. The value of α obtained here at the metastable free energy minimum corresponds to a mean square displacement (of a particle around a lattice site) which is about three times larger than that in a crystal. This is also expected more naturally since at low supercooling the particles are not sharply localized. It should be noted that the experimental observation that localization length in a glass is about 10% of the particle diameter (similar to a crystal) is a result only applicable in the deeply supercooled glassy state.

(B) In the density functional model we use for the metastable state free energy an expansion (4) around the homogeneous state. This truncated expansion is a better approximation for the free energy F since the density inhomogeneities are less abrupt here than the corresponding crystalline state. This follows from the fact that optimum choice of the density function $\rho(\mathbf{r})$ in the present model correspond to a relatively small width parameter value α for the glassy minimum as compared to that for the crystal. Similar metastable structures (corresponding to low width parameter value α) have also been confirmed [7] using the location of the amorphous lattice points from simulation data of a hard sphere system.

(C) On the observed consistency between the present model and the T_c values it is useful to note that the free energy functional chosen for the minimization in the DFT is also the one used in MCT to obtain the nonlinear equations of fluctuating hydrodynamics. Indeed, the resulting dynamic nonlinearities, quadratic in density fluctuations, give rise to the integral equations (12) used for computing T_c in the present context. The mode-coupling model presented here is the one loop version which is almost exclusively used so far for the MCT literature. On the other hand, the DFT model that we have used computes the free energy of the inhomogeneous state keeping only terms to second order in density fluctuations.

(D) We have studied here the one component Lennard-Jones system and compared our results with the simulation data for the same system as done in [36]. In recent years the glassy dynamics has also been studied by mapping the nature of the potential energy landscape (PES) of a model system consisting of a small number of particles which are interacting through a simple two body potential. For Lennard-Jones potential the binary mixture of two species [51] has been widely investigated. In such systems the Kauzmann temperature was obtained as $T_K = 0.297$ (in the Lennard-Jones units for the mixture) for packing fraction of $\eta_{BM} = 0.59$ [52]. For the one component system we obtain $T_K = 0.413$ and 0.531 (in the Lennard-Jones unit for the one component system) for packing fractions 0.56 and 0.59 respectively. The T_K values obtained here for the one component system are therefore somewhat larger than the same quantity obtained from PES studies of the binary mixture. However, this is a trend seen in the case of the other characteristic temperatures as well. Thus the mode coupling temperatures T_c for the one component system are 1.090 and 1.510 at the above two packing fractions (0.58 and 0.59 respectively). For the binary system this temperature is much lower, $T_c = 0.435$ for a packing fraction of 0.59.

Finally, in order to present a unified picture of the results of the present work, we display in figure 14 the temperatures T_c , T_g , T_0 and T_K for different values of the density ρ_0 of the Lennard-Jones liquid. The mode coupling transition temperature T_c in general lies in between the freezing point T_m and the glass transition temperature T_g while T_0 representing the free

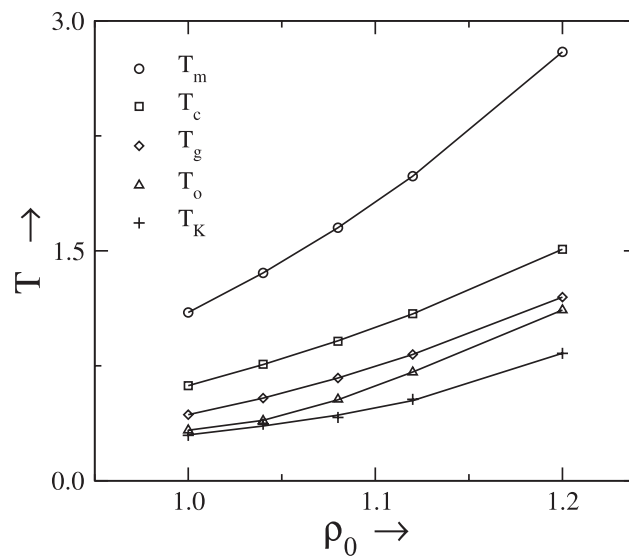


Figure 14. The characteristic temperatures (all expressed in the LJ units of ϵ/k_B) T_m , T_c , T_g , T_0 and T_K (see text) for different densities ρ_0 (in units of σ^3).

volume transition is always less than T_g . The Kauzmann temperature T_K is the lowest lying even below T_0 . The ratio of the two temperatures T_c to T_g is in the range (1.27–1.44) in our model; typical examples of fragile liquids: OTP, 1.19; Salol, 1.21; PC, 1.19. It is worth noting here that the temperatures T_g and T_c are obtained from considerations related to the dynamics. On the other hand T_0 and T_K are obtained in the present model, which is developed here from structural considerations and thus relates more to the thermodynamic aspects. The consistency of the different temperatures with the trends seen in experimental data on glass forming systems reflects the important role of both the structure as well as the dynamics in glass physics. The holes are treated here to be static and their abundance is inferred invoking the thermodynamic extremum principle. Understanding the slow dynamics of the holes or the associated free volume with the help of the generalized hydrodynamic models [53] will be of interest for future studies.

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