Fragility index of a simple liquid from structural inputs

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Received 20 May 2016, revised 30 July 2016
Accepted for publication 8 August 2016
Published 12 September 2016

Online at stacks.iop.org/JSTAT/2016/093302
doi:10.1088/1742-5468/2016/09/093302

Abstract. We make a first-principles calculation of the fragility index \( m \) of a simple liquid with known inter particle interaction. The latter determines the corresponding equilibrium structure factor which is treated as an input in the calculation. Using the density functional theory (DFT) of classical liquids, we determine the configurational entropy \( S_c \) at moderate supercooling and extrapolate this data to estimate the Kauzmann temperature \( T_K \). The relaxation time \( \tau_\alpha \) for the simple liquid has been obtained from direct solutions of the equations of fluctuating nonlinear hydrodynamics (FNH). These equations also form the basis of the mode coupling theory (MCT) for glassy dynamics. Using the Adam–Gibbs relation, we link the configurational entropy \( S_c \) to the relaxation time \( \tau_\alpha \) of the supercooled liquid. The fragility index for the supercooled liquid is estimated from analysis of the curves on the Angell plot.

Keywords: glasses (structural), metastable states, classical phase transitions, fluctuating hydrodynamics
1. Introduction

The constituent particles in a normal liquid move randomly, so that the equilibrium liquid state is isotropic in a time averaged sense. The thermodynamic equilibrium state of the liquid is described in terms of a few characteristic variables like temperature $T$, pressure $P$, volume $V$, equilibrium density $\rho_0$. The isotropic symmetry of the normal liquid state is spontaneously broken at temperature $T_m$, dependent on the pressure $P$ of the liquid, at which the liquid transforms into a crystalline state with characteristic long range order. The transformation of the liquid into crystalline solid involves absorption of latent heat.

Almost all liquids can be supercooled with varying degrees of ease, below the freezing point $T_m$ without transforming into the ordered crystalline state. The present paper focuses on the statistical mechanics of liquids below freezing. The liquid continues to remain in the amorphous state and its characteristic relaxation time drastically increases with lowering of temperature. The so called glass transition point $T_g$ which denotes the vitrification process, is defined as the temperature at which the relaxation time of the under-cooled liquid reaches the laboratory time scales. The supercooled liquid at this stage behaves like a solid with elastic properties. Unlike the transition of the liquid to the crystalline state, this transformation is not associated with any latent heat absorption. There is a drop in the specific heat due to absence of the translational degree of freedom. The free energy of the supercooled liquid does not show any discontinuous change through the glass transition. The deeply supercooled liquid remains trapped in a metastable state having free energy intermediate between the liquid and the crystalline state. Since there are a large number of available metastable structures in which the under-cooled liquid can be trapped, a considerable entropic drive is present for the process. There have been theories for the vitrification process built on...
possible scenarios of first order transitions with the special situation of a large number of available metastable states [1].

An instructive plot of the data of glassy relaxation was made by Angell [2] of relaxation time $\tau_o$ versus inverse temperature $T_g/T$ scaled with $T_g$ on a logarithmic scale. The nature of increase of relaxation time with fall of temperature in glassy systems is non-universal. At one extreme of such a plot, $\tau_o$ grows first slowly for temperature $T$ over the range $T > T'_g$, and is followed by very sharp increase within a small temperature range close to $T_g$. A more uniform increase is seen over the whole temperature range for strong liquids like B$_2$O$_3$ or SiO$_2$. This behavior has been quantified by defining a fragility parameter $m$ as the slope of the viscosity-temperature curve as [3].

$$m = \left. \frac{d\log_{10} \tau_o}{d(T_g/T)} \right|_{T=T_g} .$$

Thus for example, o-terphenyl and SiO$_2$ denote two extreme cases of fragile and strong systems with $m$ values 81 and 20 respectively. At the extreme fragile end the change of relaxation time is extremely dramatic growing by many orders of magnitude within a very narrow temperature range.

The supercooled liquid acts like a frozen solid over time scales of structural relaxation and have only vibrational motion around a frozen structure [4, 5]. The difference of the entropy of the supercooled liquid from that of the solid having only vibrational motion represents the entropy due to large scale motion of the particles and is identified as the configurational entropy $S_c$ of the liquid. A rapid disappearance of the configurational entropy of the disordered liquid occurs on approaching the glass transition point. This so called ‘entropy crisis’ poses an important question essential for our understanding the physics of glass transition and the divergence of relaxation time at $T_g$. Apart from having characteristic large viscosity, the supercooled liquid shows a discontinuity in specific heat $c_p$ at $T_g$ due to freezing of the translational degrees of freedom in the liquid. The above described features are almost universally observed in all liquids. The Kauzmann temperature $T_K$ is the temperature at which the extrapolated value of $S_c$ goes to zero and marks a possible limiting temperature for the existence of the supercooled liquid phase. Below $T_K$ we have the paradoxical situation in which the entropy of the disordered state becomes less than that of the crystal. The original hypothesis due to Kauzmann proposes eventual crystallization in the supercooled liquid at very low temperatures as a possible way out. Another possible explanation of the Kauzmann paradox could be that the simple extrapolation of high temperature result to very low temperature is not correct and the entropy difference between supercooled liquid and crystal remains finite till very low temperature [6, 7], finally going to zero only near $T = 0$.

The theory of the supercooled liquid primary deals with two broad aspects of the metastable state. These respectively refer to the thermodynamics property like the configurational entropy and the slow dynamics characteristic of the glassy state. With increased supercooling the relaxation time for the liquid sharply increases. Relaxation in the present context is meant for a typical fluctuation around the disordered liquid state at a temperature $T < T_m$. Dynamics of the deeply supercooled liquid changes over from a continuous motion of its particles to transport by activated hopping over barriers that develops at low temperature. In structural glass this occurs even without
any quenched impurities, i.e. the slow dynamics is self generated. In the Adam–Gibbs theory [8] the growth of the relaxation is linked to the configurational entropy $S_c$ of the supercooled liquid. The idea that energy barriers build up to resist molecular rearrangement in the jammed state has been used in the Adam–Gibbs theory to understand the development of very long relaxation times in the deeply supercooled state [9]. Since relaxation in the system occurs through thermally assisted hopping over the barrier ($=E_B$, say), the probability of such a jump will be controlled by the Boltzmann factor $\exp(-E_B/k_BT)$. Thus estimation of the relaxation time is closely linked to that of the energy barrier $E_B$ which must be overcome so that a local fluctuation can relax. Using these ideas it is argued [8] that the relaxation time $\tau$ is linked to the configurational entropy $S_c$ at temperature $T$ of the liquid through the relation

$$\tau = \tau_0 \exp \left( \frac{A_0}{TS_c} \right),$$

(2)

where $A_0$ is a constant. As $T \to T_K$, the configurational entropy $S_c \to 0$ and hence $\tau \to \infty$. Thus assuming a linear temperature dependence of $TS_c$ near $T_K$ we can identify $T_K$ with the temperature $T_0$ of the standard Vogel–Fulcher dependence of relaxation $\tau = \tau_0 \exp(A/(T - T_0))$ [10]. This equality between $T_0$ and $T_K$ suggests a link of deeper significance on considering the fact that the physics of the two temperatures are very different. $T_0$ represents the temperature at which the relaxation time for the supercooled liquid diverges and basically relates to the dynamics. On the other hand the Kauzmann temperature $T_K$ is related to the vanishing of the thermodynamic property of configurational entropy of the metastable liquid. Linking of the sharp increase of relaxation time to the entropy crisis signifies effects of structure on the dynamics [11].

The AG model was developed for the polymeric liquids. However the general idea is of interpreting the relaxation in a supercooled liquid at high density as a barrier crossing event. Based on this idea, we have tested here for the simple liquid, if AG relation holds between two independent properties related to the physics of supercooled liquids, namely structure and dynamics. For studying the classical liquid at densities beyond freezing point, the DFT [12–14] and the MCT [15–17] has been two primary tools. In the present paper, we use both approaches to study the properties of the supercooled liquid.

The density functional theory (DFT) is an order parameter theory [18] for freezing, using the equilibrium density as the relevant variable. The thermodynamic properties of the inhomogeneous crystalline state are obtained in terms of the corresponding properties of the homogeneous liquid state. The latter is well understood in a microscopic approach in terms of the integral equations theories [19] or simulations. A microscopic level description of the liquid is given by the interaction potential between the constituent particles. The basic characteristics of the two body potential for which a crystalline state appears (under appropriate conditions of density and temperature) include (a) a strongly repulsive part at short range and (b) an attractive part effective over long range. The Hamiltonian for the many particle system is written in a harmonic expansion around the equilibrium sites which correspond to the minimum potential energy configuration. The attractive part of the potential seemingly appears to play an important role in stabilizing the solid in a crystalline state in which the individual particles are localized around their mean positions.
In the classical DFT, the free energy of an inhomogeneous system is obtained as a functional of the one particle density \( \rho(\mathbf{x}) \) [20]. The density function is expressed in terms of a suitable set of parameters which are treated as the order parameters of the freezing transition. The free energy functional for the inhomogeneous liquid is minimized with respect to the parameters defining the density function. A very successful prescription of density distribution for the crystalline case is obtained from the superposition of Gaussian density profiles [21] centered on a lattice with long range order,

\[
\rho_0(\mathbf{r}) = \sum_i \phi_0(|\mathbf{r} - \mathbf{R}_i|)
\]

where the \( \{\mathbf{R}_i\} \) denotes the underlying lattice and the function \( \phi_0 \) is taken as the isotropic Gaussian \( \phi_0(\mathbf{r}) = (\frac{\alpha}{\pi})^{3/2}e^{-\alpha r^2} \). The thermodynamic properties of the system are computed assuming the latter to be in a single phase, i.e. either liquid or crystal. The density functional approach is mean field like since it ignores the effects of fluctuations. At a given density by locating the free energy minimum the corresponding structure is identified as the stable thermodynamic state. For high temperatures, the homogeneous liquid state is more stable while at low temperatures the crystalline state with long range order is more stable. For the simple Lennard-Jones system that we consider here, the face centered cubic (fcc) structure is more stable.

The density functional methods has been adopted for studying the thermodynamic properties of the liquid while mode coupling theories offers a microscopic model for slow dynamics of the metastable liquid approaching glass transition. In its simplest form MCT predicts a sharp dynamic transition around a temperature \( T_c \) higher than \( T_g \). This is a transition from the ergodic liquid state to a nonergodic state in which long time limits of the density correlation function does not decay to zero. Around \( T_c \), the dynamics of the liquid undergoes a qualitative change. Using only structural inputs, scaling of the non ergodicity parameter [22] and growing dynamic length scale [23, 24] have been studied around the MCT transition point.

DFT methods have been applied to model the supercooled liquid below the freezing point \( T_m \), having aperiodic structures [25–27]. For the aperiodic structure, the corresponding \( \{\mathbf{R}_i\} \) in the definition (3) for the density constitute a random structure [28–31]. Inverse of \( \alpha \) characterizes the width of the peak and therefore signifies the degree of mass localization [32] in the system. The homogeneous liquid state is characterized by the limit \( \alpha \to 0 \) and each Gaussian profile provides the same contribution in the sum at all spatial positions. The metastable states are identified as minima of the free energy, intermediate between a crystal and a homogeneous liquid state.

We use the basic equations of fluctuating nonlinear hydrodynamics which also gives rise to the mode coupling models. Recently the relaxation time of a simple liquid has been calculated [33] from a direct solution of the equations of fluctuating nonlinear hydrodynamics (FNH). These equations are also the starting point of mode coupling theory. On the other hand using the density functional methods we compute here the configurational entropy \( S_c \) in the region close to \( T_m \). In the present paper we use the temperature dependence of the relaxation time and the Adam–Gibbs relation involving the configurational entropy \( S_c \) (in the higher temperature range) to estimate the fragility index of a simple Lennard-Jones liquid. \( S_c \) is estimated using the structure of the liquid. Hence the present calculation only requires as an input the basic interaction...
potential in terms of which the structure factors are obtained. The paper is organized as follows. In section 2, we present the respective models studied for the thermodynamics and the dynamics separately. In section 3 the numerical results obtained for the configurational entropy is checked for the validity of the Adam–Gibbs relation with the use of the relaxation time. We then explore the Angell plots of the model studied. The paper ends with a discussion section.

2. Model studied

We are dealing in this paper with two types of microscopic models for the description of the metastable liquid. First, the density functional model which provides a description of the properties related to thermodynamics. Second, the equations of fluctuating nonlinear hydrodynamics for the supercooled liquid signifying the underlying conservation laws for the many particle system. We briefly describe these two approaches in this section.

2.1. The density functional model

First we briefly outline the construction of the proper free energy functional $F[\rho]$ corresponding to the ensemble in which the average density is computed. For the canonical ensemble it is the Helmholtz free energy functional $\beta F[\rho]$ which is to be minimized to identify the equilibrium state. This functional is then used to determine the appropriate parameters for the inhomogeneous density function $\rho_0(\mathbf{x})$ at equilibrium. The optimized density function is obtained by satisfying the extremum principle for $F[\rho]$. The free energy of the liquid is a sum of two parts—the ideal gas term and the interaction term, $F[\rho] = F_{id}[\rho] + F_{ex}[\rho]$. The ideal gas part of the free energy $F_{id}$ for the non-uniform density is obtained as

$$\beta F_{id}[\rho(r)] = \int \mathrm{d}\mathbf{r} \rho(r) (\ln[\Lambda^3 \rho(r)] - 1).$$

$\Lambda$ represents the thermal wavelength appearing due to the momentum variable integration in the partition function. The interaction part $F_{ex}[\rho(\mathbf{x})]$ is evaluated using the standard expression for the Ramakrishnan–Yussouff (RY) functional [18] involving a functional Taylor series expansion in terms of the density fluctuation $\delta \rho(r) = \rho(r) - \rho_0$ around a reference density $\rho_0$.

$$F_{ex}[\rho] = F_{ex}[\rho_0] - \int \mathrm{d}\mathbf{x}_1 \psi^{(1)}(\mathbf{x}_1; \rho_0)\delta \rho(\mathbf{x}) - \frac{1}{2} \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2 \psi^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \rho_0)\delta \rho(\mathbf{x}_1)\delta \rho(\mathbf{x}_2) + \ldots$$

(5)

The series involve the functions $\psi^{(i)}(\mathbf{x}; \rho_0)$’s defined in (6) at $\rho(\mathbf{x}) = \rho_0$. We use the following definitions for the direct correlation functions $\psi^{(i)}$s as the successive functional derivatives of $F_{ex}$ evaluated at density $\rho_0$,

$$\psi^{(i)}(\mathbf{x}_1, \ldots, \mathbf{x}_i; \rho_0) = \left( \frac{\delta^i F_{ex}}{\delta \rho(\mathbf{x}_1)\ldots\delta \rho(\mathbf{x}_i)} \right)_{\rho = \rho_0}$$

(6)
For practical calculations one usually adopts the simplest approximation keeping only up to the second order term \( i = 2 \) in the expansion for the direct correlation function. In general the reference density \( \rho_0(\mathbf{x}) \) can itself be inhomogeneous. If the reference state is a uniform homogeneous liquid, \( \rho_0 \) will be independent of position and the above direct correlation functions will be those for the uniform state.

For identifying the equilibrium state, the extremum principle for \( F[\rho] \) in the canonical ensemble is applied by setting the corresponding functional derivative with respect to \( \rho \) zero for \( \rho(\mathbf{x}) = \rho_0(\mathbf{x}) \) where \( \rho_0(\mathbf{x}) \) represents the equilibrium density.

\[
\ln[\lambda^3 \rho_0(\mathbf{x})] - c^{(1)}(\mathbf{x}; \rho_0(\mathbf{x})) + \beta \phi(\mathbf{x}) = 0, \tag{7}
\]

where \( \phi(\mathbf{x}) \) is the external potential. Using the result (7) we obtain for the equilibrium density \( \rho_0(\mathbf{x}) \)

\[
\rho_0(\mathbf{x}) = z \exp[-\beta \phi(\mathbf{x}) + c^{(1)}(\mathbf{x}; \rho_0(\mathbf{x}))], \tag{8}
\]

where \( z = \lambda^{-3} \) in this case. The quantity \( c^{(1)}(\mathbf{x}; \rho_0(\mathbf{x})) \) acts as a one body potential due to the interaction between the fluid particles. The higher order direct correlation functions are defined in terms of functional derivatives of \( c^{(1)} \) with respect to \( \rho(\mathbf{x}) \). Making a simple Taylor expansion for \( c^{(1)}(\mathbf{x}; \rho_0(\mathbf{x})) \) around its value \( c_l \) in the uniform liquid state of density \( \rho_0 \), we obtain,

\[
c^{(1)}[\mathbf{x}; \rho_0(\mathbf{x})] = c_l(\rho_0) + \int d\mathbf{x}_2 c^{(2)}(\mathbf{x}_1, \mathbf{x}_2) \delta \rho_0(\mathbf{x}_2) + \frac{1}{2} \int d\mathbf{x}_2 d\mathbf{x}_3 c^{(3)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \delta \rho_0(\mathbf{x}_2) \delta \rho_0(\mathbf{x}_3) + \ldots \tag{9}
\]

where \( \delta \rho_0(\mathbf{x}) = \rho_0(\mathbf{x}) - \rho_0 \) is the fluctuation of the equilibrium density in the inhomogeneous solid state from that of the liquid state. The two point correlation function \( c^{(2)}(\mathbf{x}_1, \mathbf{x}_2) \) is related to the pair correlation function \( g^{(2)}(\mathbf{x}_1, \mathbf{x}_2) \) in the fluid by a relation which reduces to the Ornstein–Zernike relation for the uniform liquid.

For the uniform liquid in absence of any external field we have from equation (8) for the uniform density \( \rho_0 = z \exp(c_l) \). The (equilibrium) inhomogeneous density function \( \rho_0(\mathbf{x}) \) is then obtained in terms of the corresponding one particle direct correlation function \( c^{(1)}(\mathbf{r}) \),

\[
\rho_0(\mathbf{x}) = \rho_0 \exp\{ c^{(1)}(\mathbf{x}; \rho_0(\mathbf{x})) - c_l - \beta \phi(\mathbf{x}) \}. \tag{10}
\]

The equilibrium density is therefore obtained as

\[
\rho_0(\mathbf{x}) = \bar{\rho}_0(\mathbf{x}) \exp\left[ \int d\mathbf{x}_2 c^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \rho_0) \delta \rho_0(\mathbf{x}_2) \right] \tag{11}
\]

where we identify \( \bar{\rho}_0(\mathbf{x}) = z \exp[-\beta \phi(\mathbf{x}) + c_l] = \rho_0 \exp[-\beta \phi(\mathbf{x})] \). For equation (11) the trivial solution is then the uniform density \( \rho(\mathbf{x}) = \rho_0 \) in absence of any external field \( \phi \).

The solution of equation (11) is the starting point for the subsequent analysis for testing the possibility of an inhomogeneous density state. The two point kernel function \( c^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \rho_0) \) which is defined in terms of the functional derivative of the one body potential \( c^{(1)} \) is required to completely specify the equation (11) for the inhomogeneous density. The difference between the free energy functionals respectively corresponding to the inhomogeneous state with density \( \rho_0(\mathbf{x}) \) and the homogeneous liquid state with density \( \rho_0 \) (with an external potential \( \phi(\mathbf{x}) \) coupling to the density field) is obtained as,
\[ \Delta F = F[\rho_0(\mathbf{x})] - F[\rho_0] = \Delta F_{\text{id}}[\rho_0(\mathbf{x})] + \Delta F_{\text{ex}}[\rho_0(\mathbf{x})] + \int d\mathbf{x}_i (\rho_0(x_i) - \rho_0) \phi(x_i). \] (12)

The difference \( \Delta F_{\text{id}} \) in the ideal gas part of the free energy is directly calculated from (A.2). The difference \( \Delta F_{\text{ex}} = F_{\text{ex}}[\rho_0(\mathbf{x})] - F_{\text{ex}}[\rho_0] \) between the excess free energies of the liquid and solid states is expressed as a functional Taylor expansion in the density fluctuations \( \delta \rho_0(\mathbf{x}) = \rho_0(\mathbf{x}) - \rho_0 \) from (5). Using these results, we obtain the free energy difference as

\[ \beta \Delta F = \int d\mathbf{x}_i \left[ \rho_0(\mathbf{x}_i) \ln \left( \frac{\rho_0(\mathbf{x}_i)}{\rho_0} \right) - \frac{1}{2} \int d\mathbf{x}_2 c^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \rho_0) \delta \rho_0(\mathbf{x}_2) \delta \rho_0(\mathbf{x}_1) \right]. \] (13)

In reaching the above equation we have applied the extremum condition (7). The optimum choice for the density function \( \rho_0(\mathbf{x}) \) follows from minimizing \( \Delta F \) with respect to the parameter \( \alpha \) corresponding to the definition (3) for the density distribution for structures \( \{ \mathbf{R}_i \} \). For \( \alpha \to 0 \), the value of \( \Delta F \) is zero by construction. This follows directly from \( \rho_0(\mathbf{x}) \to \rho_0 \) as \( \alpha \to 0 \) and hence both ideal and excess parts of \( \Delta F \) separately vanish.

In this work we take two different choices for \( \{ \mathbf{R}_i \} \), the crystalline lattice with FCC structure and the amorphous lattice with random structure. The latter is described in terms of the Bernal pair correlation function. The corresponding values of \( \Delta F \) are denoted as

\[ \Delta F_{\text{C}} = F_{\text{C}} - F_{\text{L}}, \quad \text{and} \quad \Delta F_{\text{A}} = F_{\text{A}} - F_{\text{L}}, \] (14)

where \( F_{\text{L}}, F_{\text{A}}, \text{and} F_{\text{C}} \) respectively denote the free energies of the uniform liquid (for \( \alpha \to 0 \)), crystalline, and the amorphous states. Thus we have

\[ F_{\text{A}} - F_{\text{C}} = \Delta F_{\text{A}} - \Delta F_{\text{C}} \equiv \Delta F. \] (15)

Using standard thermodynamic definition the corresponding entropies are obtained by taking derivatives with respect to temperature.

\[ S_{\text{amorphous}} - S_{\text{crystal}} = \frac{\partial}{\partial T}(\Delta F(T)). \] (16)

It is important to note here that the \( F_{\text{A}} \) in equation (14) as obtained in the DFT approach should not be confused as a the free energy for a particular amorphous configuration. In the present interpretation it represents the free energy of the glassy metastable state at a given temperature. This is justified since in calculating the amorphous state free energy, the information of the amorphous structure is not incorporated in the model in terms of a single individual aperiodic configuration, but in terms of a pair correlation function which is averaged over all such configurations. The present calculation of \( S_c \) is purely based on taking the DFT calculation of the free energy for the amorphous state in the same spirit as the thermodynamic analogue for the metastable state. The present definition therefore is analogous to an experimental interpretation of the DFT.

2.2. Model for the dynamics

The slow dynamics of a dense liquid is generally studied in terms of the correlation of density fluctuations which occur in the strongly interacting many particle system. The
structural relaxation is best understood in terms of the two point dynamic correlation function $C(q, t_1, t_2)$ of density fluctuations at times $t_1$ and $t_2$, corresponding to wave vector $q$. The correlation function is defined in the normalized form

$$
C(q, t_1, t_2) = \frac{\langle \delta \rho(q, t_1) \delta \rho(-q, t_2) \rangle}{\langle \delta \rho(q, t_2) \delta \rho(-q, t_2) \rangle}.
$$

(17)

For the equilibrium state, time translational invariance holds and $C(t_1, t_2)$ is a function of $(t_1 - t_2)$ only. The long time limit of the time correlation of density fluctuations is treated as an order parameter in the mode coupling theory (MCT) of glassy dynamics. This quantity, termed as the nonergodicity parameter (NEP), makes a discontinuous jump from being zero in the liquid state to a nonzero positive value at the ergodic-nonergodic (ENE) transition of MCT. The corresponding temperature $T_c$ identified with the sharp transition signifies a point at which a qualitative change occurs in the moderately supercooled regime. $T_c$ lies in a temperature range between the freezing temperature $T_m$ and the glass transition temperature $T_g$. The sharp ENE transition is smoothed off in a complete analysis of the nonlinearities in the equations which control the dynamics of density fluctuations. However the qualitative change in the dynamics in the initial stages of supercooling, around $T_c$ are described in terms of the basic equations of FNH. The model equations of MCT also follows from these equation which are plausible generalizations of equations of hydrodynamics extended to small wave lengths. These equations have been solved numerically [33, 34] and the relaxation times obtained are in good agreement with simulations results on similar systems [33].

For an isotropic liquid, the model equations of FNH for the mass density $\rho$ and momentum density $g$ [35] in the simplest form are as follows :

$$
\frac{\partial \rho}{\partial t} + \nabla \cdot g = 0,
$$

(18)

$$
\frac{\partial g_i}{\partial t} + \rho \nabla_i f(r, t) - L^0_{ij} \frac{g_j}{\rho} = \theta_i.
$$

(19)

The correlations of the Gaussian noise $\theta_i$ are related to the bare damping matrix $L^0_{ij}$ [36],

$$
\langle \theta_i(x, t) \theta_j(x' t') \rangle = 2k_B T L^0_{ij} \delta(t - t') \delta(x - x').
$$

(20)

For an isotropic liquid, the bare transport coefficients are obtained as,

$$
L^0_{ij} = (\zeta_0 + \eta_0/3) \delta_{ij} \nabla^2 + \xi_0 \nabla_i \nabla_j
$$

(21)

where $\zeta_0$ and $\xi_0$ respectively denote the bare bulk and shear viscosities. For the glassy dynamics we focus on the coupling of slowly decaying density fluctuations present in the pressure functional, represented by the second term on the LHS of equation (19). The nonlinear contribution in this term is obtained with the function $f(r, t)$. The latter is presented as a convolution

$$
f(r, t) = m^{-1} \int d r' c(r - r') \delta \rho(r', t).
$$

(22)
If we replace $\rho$ by $\rho_0$ in the LHS of equation (19) then we have a dynamics linearized in density fluctuations. The above described FNH equations are solved numerically on a grid. The direct correlation function $c(r)$ is used as an input for solving the FNH equations and the noise averaged correlation function $C(q,t)$ of density fluctuations are obtained [33].

3. Numerical results

In DFT, the free energy is expressed as a functional of the density $\rho(x)$ which incorporates two key properties of the solid state. First, the extent of mass localization in the system is denoted by the width parameter $\alpha$ defined in the equation (3). Second, the underlying lattice $\{R_i\}$ on which the Gaussian density profiles are to be centered. Both of these properties are treated as control parameters of DFT.

For our analysis, we consider here a classical system of $N$ particles, each of mass $m$ interacting with a Lennard-Jones potential $\frac{\epsilon}{\sigma^6}$.

\begin{equation}
\sigma^2 = -\epsilon u(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right].
\end{equation}

The basic interaction potential in equation (23) defines the length scale $\sigma$ and energy scale $\epsilon$ used in defining the units of density and temperature. The equilibrium density and the temperature of the LJ system in the present paper will be respectively expressed in units of $\sigma^{-3}$ and $\epsilon/k_B$. The structure of the corresponding homogeneous liquid, denoted by $c(r)$ is a required input in the calculation. For the LJ potential, the direct correlation function of the uniform liquid is obtained using the bridge function method [37, 38]. The thermodynamic properties of the supercooled liquid are obtained using the constant NVT ensemble of $N$ particles interacting with the LJ potential in volume $V$ and has a constant temperature $T$. In figure 1 we show the direct correlation function $c(r)$ obtained for density $\rho \sigma^2 = 1.1$. The corresponding temperatures are $k_B T/\epsilon = 0.8$ and 1.0. Next, we consider the distribution of particle sites $\{R_i\}$. In case of crystal, FCC lattice serves as the particle sites. For the amorphous glassy states, the centers for the Gaussian density profiles $\{R_i\}$ in the expression (3) for the density function are assumed to be distributed on a random lattice. A standard procedure generally followed [25, 39, 40] here to obtain the random structure is to use the $g_B(R)$ corresponding to the Bernal’s packing [41] which is generated through the Bennett’s algorithm [42]. We use the random structure $g_s(R)$ through the following relation [39]

\begin{equation}
g_s(R) = g_B \left[\left(\frac{\eta}{\eta_0}\right)^{1/3} R\right],
\end{equation}

where $\eta$ denotes the average packing fraction. In the above relation $\eta_0$ is used as a scaling parameter for the structure such that at $\eta = \eta_0$ Bernal’s structure $g_B(R)$ is reproduced. The mapping of the function from $g_s(R)$ to $g_B(\eta/\eta_0)^{1/3} R)$ makes the structure represented by $g_s$ to become more spread apart with increasing $\eta_0$ at a fixed packing fraction $\eta(<\eta_0)$. The role of the $\eta_0$ on the free energy landscape plays a crucial role in this work. We display in figure 2 the Bernal’s random structure. In this regard it should be noted that for a hard sphere system identification of the most closely packed random
structure is somewhat anomalous [43]. In the present context, however, the Bernal structure is simply applied as a tool to evaluate the free energy for an inhomogeneous density profile centered at the random set of lattice points. The same free energy functional when tested with random structures obtained from computer simulation studies [44] also identified similar metastable minima with low degree of mass localization.

Using the above formulas and the input structure for the uniform liquid in terms of $c(r)$ and the random structure \{R_i\} from the Bernal pair correlation function, the free energy is calculated as a function of the width parameter $\alpha$. The free energy minimum at a given temperature $T < T_m$ corresponds to a metastable state with amorphous structure lying in the supercooled regime. The free energy minimization with respect to $\alpha$ is
displayed in figure 3 for two specific cases displaying the crystalline and the amorphous metastable state. Note that the metastable amorphous structure corresponds to a much lower degree of mass localization compared to the crystalline state. The difference of the free energy of the amorphous or the crystalline state from that of the uniform liquid state are respectively denoted by $\Delta F_A$ and $\Delta F_C$. The signs of these quantities mark the relative stability of the respective inhomogeneous state with respect to the homogeneous liquid state. In figure 4 we show that $\Delta F_C$ become negative at temperature $T_m = 0.98$ (shown with an arrow) marking the freezing point. The amorphous state becomes metastable compared to the liquid state at a little lower temperature. We choose $\eta_0 = 0.67$ for results of figures 3 and 4. For different choices of density $\rho_0\sigma^3$ of the liquid, we obtain the corresponding $T_m$ as shown in figure 5.

3.1. Configurational entropy

The metastable amorphous state distinct from the uniform liquid state, is identified by locating the intermediate minimum of the corresponding free energy with respect to the mass localization parameter $\alpha$. The latter determines the width of the Gaussian density profiles in equation (3). For different temperatures, using equation (13) we now find the optimum free energy differences $\Delta F_A$ and $\Delta F_C$, respectively corresponding to the amorphous (metastable) and the crystalline (thermodynamically stable) structure. Here $\Delta F$ follows from equation (13). For the metastable states we use the Bernal’s structure to construct the random lattice $\{\mathbf{R}_i\}$. Different set of lattice points are produced by varying the scaling parameter $\eta_0$ introduced in defining the pair correlation function for the random structure. The set of $\eta_0$ values are taken as synonymous to different species of glass forming materials. The configurational entropy $S_c$ in the temperature range close to $T_c$ is obtained as

doi:10.1088/1742-5468/2016/09/093302
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\[ S_{\text{amorphous}} - S_{\text{vib}} \]

where \( S_{\text{vib}} \) gives the vibrational entropy for the amorphous state. Following the general notion the vibrational properties of crystal and corresponding glassy-state are quite similar. Consequently, the experimentalists have approximately determined the configurational entropy by subtracting the crystalline entropy from the entropy of the liquid.

\[ S_c = S_{\text{amorphous}} - S_{\text{crystal}} \]

which can be computed easily using equation (16).

In the numerical calculation, by using the density functional value of \( F \), we obtain the configurational entropy \( S_c \) of the supercooled liquid state. The difference between

**Figure 4.** Difference of the free energy \( \Delta f \) of the amorphous glassy state (solid) and fcc crystalline state (dashed) respectively from that of the uniform liquid versus temperature \( k_B T/\epsilon \), at constant density \( \rho_0 \sigma^3 = 1.1 \).

**Figure 5.** The freezing temperature \( T_m \) (in units of \( \epsilon / k_B \)) versus density \( \rho_0 \sigma^3 \).
the entropies of the amorphous state with a weak degree of mass localization \( (\alpha \sigma^2 \sim 10^1) \) and the crystalline state with sharply localized mass distribution \( (\alpha \sigma^2 \sim 10^3) \) is taken here as the configurational entropy. At constant density \( \rho \sigma^3 = 1.1 \), we obtain the \( S_c \) for a set of values for the parameter \( \eta_0 = 0.67, 0.68, 0.69, \) and 0.70. The configurational entropy studied in this density functional model is extrapolated beyond the studied temperature range as shown in figure 6 with the form

\[
S_c = S_0 \left( 1 - \frac{T_K}{T} \right). \tag{27}
\]

For various \( \eta_0 \), we obtain by fitting the \( S_c \) to the above form the corresponding \( T_K \) as well as \( S_0 \). To test the Adam–Gibbs relation we use the result for the relaxation time \( \tau \) obtained from the solution of the FNH equations \([33]\). The input structure factor for the liquid used in solving the FNH equations are same as those used in computing the \( S_c \) in the density functional models. The relaxation time \( \tau \) is then linked to the configurational entropy \( S_c \) via AG relation so that the \( \ln(\tau/\eta_0) \) versus \( 1/T S_c \) plot is taken as the best fit to a straight line. This is displayed in figure 7. Fitting each set of the configurational entropy data (corresponding to a specific choice of the parameter \( \eta_0 \)) the Adam–Gibbs line and hence the slope \( A_0 \) for each \( \eta_0 \) value is obtained. Thus \( A_0, S_0 \) and \( T_K \) are obtained for each \( \eta_0 \). Using these we determine for the system characterized by the structure parameter \( \eta_0 \), the corresponding fragility index \( m \) on the Angell plot.

### 3.2. Angell plot

The plot of the glassy relaxation time \( \tau \) (on a logarithmic scale) versus the corresponding inverse temperature \( T_g/T \), (scaled with the glass transition temperature \( T_g \)) is referred to as the Angell plot \([2, 45]\). Here the temperature \( T_g \) is defined to be the one at which the relaxation time grows by a chosen order of magnitudes \( B \) (say) compared

---

**Figure 6.** Configurational entropy \( S_c \) versus \( \bar{T} (= T/T_m) \) at \( \rho_0^* = 1.1 \) for amorphous structure as given by \( \eta_0 = .69 \). The data is extrapolated by a fit (27) to obtain the corresponding \( T_K \).
to its short time value for any specific system. The quantity $B$ is same for all materials and generally it is chosen to be 16 [3, 46]. A given curve on the Angell plot is linked with the configurational entropy $S_c$ of the system using the Adam–Gibbs relation.

As indicated above, we have already estimated $T_K$ independently from the structural data, i.e. by an extrapolation of the fit of the configurational entropy data obtained at higher $T$ (near $T_m$) with the function given by (27). Using this form of $S_c$ the Adam–Gibbs relation obtains

$$
\tau = \tau_0 \exp \left( \frac{A_0}{S_0 (T - T_K)} \right).
$$

(28)

The relaxation time data is expressed as a function of the scaled temperature $x = T_g / T$ with the relation,

$$
\ln \left( \frac{\tau}{\tau_0} \right) = C_0 \frac{x}{\kappa - x}.
$$

(29)

We have defined the quantities $C_0$ and $\kappa$ respectively as

$$
C_0 = \frac{A_0}{S_0 T_K}
$$

(30)

$$
\kappa = T_g / T_K.
$$

(31)

Using the relaxation data obtained from the solution of FNH equations [33], the constant $C_0$ is calculated. For every choice of the parameter $\eta_0$ which characterize the structure of a particular glass forming system in the DFT model, a corresponding $C_0$ is obtained. At $T = T_g$, i.e. $x = 1$ we obtain,
The fragility index $m$ defined in equation (1) is obtained by calculating the derivative of the Angell curve given in equation (29) at $T = T_k$, i.e. $x = 1$.

$$m = \frac{\kappa C_0}{(\kappa - 1)^2}. \tag{33}$$

In figure 8 we display the fragility index $m$ versus the corresponding $\eta_0$ characterizing the different structures. The figure shows that less fragile systems have higher characteristic $\eta_0$ values, making the Gaussian centers more spread out. This represents a structure with sharply localized particles and is more robust for the stronger liquid in which structural degradation is hindered. To summarize the procedure, we read $S_0$ and $T_K$ from the extrapolation of $S_c$ as shown in figure 6. $A_0$ is obtained as a fitting parameter in figure 7. The latter involves fitting respective data of relaxation time (from solution of FNH equations) and configurational entropy (from DFT) with the Adam–Gibbs relation. Using these, the constant $C_0$ defined in equation (30) is obtained for the corresponding $\eta_0$. For a chosen value of $B$, the relation (32) determines the $\kappa$ for a corresponding $C_0$. Each pair of $\{C_0, \kappa\}$ is obtained for a chosen $\eta_0$. The underlying structures $\{R_i\}$ used in computing the configurational entropy $S_c$ of the supercooled liquid correspond to chosen $\eta_0$ defined in equation (24).

Using the above result an Angell-plot of $\ln[\tau/\eta_0]$ versus $x$ corresponding to a chosen $B = 16$ is shown in figure 9. The different curves are characterized by respective values of fragility $m$. The fragility is obtained using equation (33). The different curves correspond to a set of $\eta_0$ values. On the same plot we display the $\tau/\eta_0$ data for the Lennard-Jones system obtained from the solutions of the equations of FNH. The fragility $m$ for any particular curve on the Angell plot in figure 9 is determined by the $\{\kappa, C_0\}$. Thus we obtain $m$ for a chosen value of $\eta_0$. The high temperature part
(low values of $x$) of each of the curves on the Angell plot in figure 9 fits well to a power law divergence $(T - T_{c})^{-a}$, with a corresponding set of $(T_{c}, a)$. For each curve on the Angell plot the corresponding glass transition temperature $T_{g}$ is different. Since $T_{K}$ is known, $T_{g}$ is obtained using equation (32). The ratio $T_{c}/T_{g}$ versus fragility index $m$ is shown in figure 10 and the exponent $a$ versus $m$ is shown in the inset. The agreement with experimental results of $T_{c}/T_{g} = 1.2$ [15] (see p 817, table I) is reached for $m = 117$ corresponding to choosing an underlying structure with $\eta_{0} = .69$. 

\[ \text{Figure 9.} \text{ The Angell plot of the relaxation data. Also shown in the figure by dashed lines the corresponding power law fit predicted from the MCT } (T - T_{c})^{-a}. \text{ The points shown are for } \eta_{0} = 0.70 \text{ (circles), 0.69 (squares), 0.68 (diamonds), 0.67 (triangles).} \]

\[ \text{Figure 10.} \text{ } T_{c}/T_{g} \text{ versus fragility index } m. \text{ The arrow indicates the point at which the ratio is 1.3. The inset shows the power law exponent } a \text{ (see text) versus fragility index } m. \]
4. Discussion

In all its simplicity, the AG relation glues together two important basic properties of glassy systems, respectively related to the dynamics and the thermodynamics, making the liquid’s relaxation time to be driven by the configurational entropy. The Adam–Gibbs relation equation (28) shows that as the configurational entropy $S_c$ becomes zero, the relaxation time $\tau$ diverges. According to the Adam–Gibbs hypothesis, the relaxation of the undercooled liquids should involve ‘cooperatively rearranging regions (CRR)’. The CRRs define the smallest size of system of rearranging particles such that there is no smaller groups of particles that would independently rearrange to create a new configuration. However, with temperature the size of the CRRs changes and is linked to an intrinsic length scale. When temperature decreases, the motion of particles gets cooperative on a growing length scale. The slowdown of dynamics is therefore taken to be a collective phenomenon. From the number of possibilities of forming a CRRs of given size the configurational entropy $S_c$ is obtained. By interpreting the relaxation in the deeply supercooled state as crossing the corresponding energy barrier, the Adam–Gibbs relation follows. Freed and co-workers assessed [47–49] the limitations of the Adam–Gibbs and GibbsDiMarzio models and introduced the generalized entropy theory of glass formation. Their model describe the fluid behavior within the temperature range above the glass transition temperature $T_g$, where the process of glass formation can be understood in terms of equilibrium thermodynamic description. With this more realistic description of the thermodynamics of polymeric systems is achieved using the lattice cluster theory (LCT) which is a generalization of the Flory theory for semi-flexible chains. The chain backbone and side groups are treated as the central variables affecting glass formation. The influence of the short range correlations in these models is imparted by chain connectivity, semi-flexibility, and monomer molecular structure.

The simple form of free energy functional used in DFT shows that below freezing point $T_m$, there are inhomogeneous states metastable between liquid and crystal. Extending the ideas of the DFT, we compute the entropy $S$ for the inhomogeneous state. The vibrational entropy $S_v$ of the amorphous state is identified with the entropy of the corresponding crystalline state. We approximate the configurational entropy $S_c$ at the supercooled temperatures $T < T_m$ by subtracting the vibrational part from the total entropy $S$. The configurational entropy $S_c$ calculated here is at relatively higher temperatures $T (< T_m)$, close to the freezing point. $S_c$ is extrapolated to obtain the Kauzmann temperature $T_K$. There is no unique definition for $S_c$ and estimation of the configurational entropy has been done using various approaches [50, 51]. Microscopic models using replica approach [52–54] for describing the supercooled liquids has been built on starting from only the interaction potential. More recently, Lennard-Jones systems has been studied by Bomont et. al. [55] by considering a mixture containing two replicas and the overlap function of the two replicas were studied in the hypernetted chain (HNC) approximation [19]. The observed Kauzmann temperature in this model for density $\rho^* = 1.1$ is $T_{K}^* = .31$, and is comparable to our result $T_{K}^* = .34$ for the same density. The DFT calculation involves extra input structural parameter like $\eta_0$ which is .70 in this case. In the present work we have adopted methods which are similar to those used in treatment of experimental data. The present scheme is directly feasible and keeps consistency with the AG approach which constitutes a key element in the
present work. The system we consider here are simple Lennard-Jones liquid and application of the definition is straightforward.

For very low temperatures, close to $T_g$, the structural information for the uniform liquid is not good enough to obtain the free energy using the simple DFT used here. Density fluctuations are expected to be much stronger since the deeply supercooled state is strongly heterogeneous. Extending a low order expansion in density fluctuations for computing the free energy at low temperatures is therefore not reliable. For hard sphere system there are methods like MWDA [56, 57] to consider strongly inhomogeneous states. It is important to note here that the metastable free energy minima for the inhomogeneous states we consider here, correspond to a low degree of mass localization ($\alpha \sigma^2 < 20$). Hence keeping up to second order in the functional expansion (5) for the free energy in terms of density fluctuations is a reasonable approximation. If the metastable minimum of the free energy correspond to large $\alpha$, a low order perturbative approach would not be very accurate. In such cases weighted density functional approximations [58] have been applied to compute the free energy of the amorphous state. For the Lennard-Jones system, the DFT is formulated in terms of an equivalent hard sphere system whose diameter changes with the temperature. In our model such mappings are not needed and temperature dependence of the free energy directly comes from that of the static correlation $c^{(2)}(x_i, x_j)$ which appear in the free energy expression (13).

The parameter $\eta_0$ plays an interesting role in the present DFT calculation. The various curves shown on the Angell plot in figure 9, corresponds to $C_0$ values all of which are obtained by varying the structural parameter $\eta_0$ but keeping the relaxation data same as that for the Lennard-Jones system. The parameter $\eta_0$, used to generate the different structures, may be identified as a representing various glass forming systems. This dependence can therefore be further explored with a different sets of relaxation data for a wider variety of glass forming materials. The variation of the $T_c$ and the power law exponent $a$ with the fragility index $m$ obtained in the present work is in agreement with expected non universality of these quantities in the standard mode coupling theory. In the present work we are able to link the structural parameter $\eta_0$ for the amorphous state to the fragility index $m$ for the supercooled liquid.

In the present work, we have estimated the structural contributions to dynamics using the DFT approach. This has been widely adopted in studying the freezing transition and the dynamics of supercooled liquids [59, 60] transforming in to a glassy state. For the simple Lennard-Jones potential, both structural and dynamic properties are obtained through first-principles calculations here. Comparing the results obtained from dynamic and structural sides, we observe that the agreement with the AG relation is reasonable. It is important to note here that the present calculation of $S_c$ using DFT is based on an interpretation of the DFT formulation different from some of the other works [29, 30]. The free energy calculation done here with the Bernal pair function, do not refer to one single aperiodic distribution. Rather, we interpret the input structural information being averaged over all such possibilities. With this $S_c$ is computed from equations (14) and (16). The computed value of the specific thermodynamic property should only be linked with an experimentally measured value of the corresponding physical quantity. We have assumed that in the high temperature range, we can extend classical DFT in this way and such an approach with density as an order parameter holds. We work with a coarse grained density to calculate the thermodynamic free energy albeit for a meta-stable
state. The corresponding relaxation times are also calculated from direct solution of
equations of generalized hydrodynamics here, it should be noted. This paper tests if the
structural calculation can be linked to the dynamic calculation through Adam–Gibbs
type relation. For a more microscopic approach using DFT, one has to first develop
the proper mathematical model along, say the ideas of [52–54] and take in to account the
spontaneous ergodicity breaking at low temperatures. Unfortunately this has not been
achieved yet with the simple free energy functional that we adopt here.

In standard self-consistent MCT, the density auto correlation function $C(t)$ is calculated
by solving the corresponding (deterministic) nonlinear integral equation, obtained
by keeping leading order contributions of the memory functions. The order here refers
to a perturbative formulation of the dynamics of dense liquids. The simplest model
of this MCT formulation predicts a sharp ENE (ergodicity-nonergodicity) transition
in the liquid beyond a critical density and gives rise to very long relaxation time $\tau$
near the transition point. In the present work however $\tau$ is estimated from the corre-
sponding $C(t)$ obtained by directly solving the stochastic equations of fluctuating non-
linear hydrodynamics (FNH) having all the relevant nonlinearities. It includes the $1/\rho$
type term which gives rise to the ergodicity restoring mechanisms of extended MCT.
Here the correlations are decaying to zero below the so called ENE transition point of
simple MCT. For the hard sphere system, the two step relaxation behavior and the
scaling properties of simple MCT models gets masked [33] by the ergodicity restoring
processes to a large extent. The $\tau$ obtained from the full correlation function shows
approaching divergence at much higher packing (density). This has been seen for both
two point and four point functions [33, 61]. It is important to note in this respect that
the present set of FNH equations are obtained with simple Ramakrishnan–Yussouff
type free energy functional and give rise to simple MCT as a first approximation. This
approaching transition at low temperatures has been identified often with the Replica
symmetry breaking (RSB) transition [62] characteristic of a class of spin-glass models.
For the $p$-spin models such transition has been predicted [63, 64] and more recently has
also been linked to structural glass transitions [65] in higher dimensional systems. The
low temperature dynamics of the structural model formulated using replicated liquid
[52] would be an useful next step [54, 66].

Acknowledgment

LP acknowledges CSIR, India for financial support. SPD acknowledges support under
grant 2011/37P/47/BRNS.

Appendix. Evaluation of free energy

To perform a numerical evaluation of the equation (4), we first express the free energy
in terms of the inhomogeneous density profiles represented by the Gaussian of equa-
tion (3). The ideal part free energy is now

$$\beta F_{id} = \int d\mathbf{r} \sum_{i=1}^{N} \phi_0(\mathbf{r} - \mathbf{R}_i) \left[ \ln \left( \frac{1}{N} \sum_{j=1}^{N} \phi_0(\mathbf{r} - \mathbf{R}_j) \right) - 1 \right].$$

(A.1)
In the free energy calculation, $\alpha$ serves as a variational parameter and the minimization will be performed w.r.t. this parameter. While terms involving the lattice sites $\{R_i\}$ in the expression are taken into account through a proper counting of the sites enclosed within corresponding shells. The number of particle sites within a shell of radii $R$ and $R + dR$ is taken to be $4\pi R^2 \rho g(R)dR$. Thus the ideal gas free energy is

$$\beta F_{\text{id}}N = \int d\mathbf{r} \phi_0(\mathbf{r}) \left[ \ln \left( \lambda^2 \int d\mathbf{R} \phi_0(\mathbf{r} - \mathbf{R})(\delta(\mathbf{R}) + \rho_0 g_0(\mathbf{R})) \right) - 1 \right]. \quad (A.2)$$

With substitution of the gaussian form $\phi(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{3/2} \exp(-\alpha r^2)$, in the above expression the angular part $(\theta, \phi)$ integrations of $\mathbf{R}$ would deduce to

$$\int d\mathbf{R} e^{-\alpha(r-R)^2} g_0(\mathbf{R}) = \frac{\pi}{\alpha r} \int dR g(B_0(R)) \left[ e^{-\alpha(r-R)^2} - e^{-\alpha(r+R)^2} \right]. \quad (A.3)$$

Using this result the above equation $(A.2)$ reduces to the following form.

$$\beta F_{\text{id}}N = \frac{3}{2} \ln \left( \lambda^2 \frac{\alpha}{\pi} \right) - 1 + \left( \frac{\alpha}{\pi} \right)^{3/2} 4\pi \int dr^2 e^{-\alpha r^2} \times \ln \left[ e^{-\alpha r^2} + \frac{\pi \gamma_0^2}{\alpha r} \int dR \ g_B(R) \rho_0 \{ e^{-\alpha(r-R)^2} - e^{-\alpha(r+R)^2} \} \right], \quad (A.4)$$

where $\gamma_0 = (\eta_0/\eta)^{1/3}$ represents the scaling factor introduced in equation $(24)$. In reaching the above result in the integral $(A.4)$, the pair correlation function $g(r)$ is approximated in terms of the Bernal pair function $g_B(R)$ using the scaling relation $(24)$ which involve the parameter $\eta_0$. Furthermore, we have changed the variable $R$ in the pair correlation function $g_B$ to $R$ where $R = \gamma_0 \tilde{R}$. We compute the ideal gas part free energy per particle by supplying the Bernal’s random structure $g_B$ in the equation $(A.4)$. In the asymptotic limit of the large $\alpha$, the Gaussian density profiles are sharply peaked around the respective lattice sites. Assuming that there is no overlap of the Gaussian profiles around the different sites, the ideal gas part of the free energy is well approximated with the asymptotic formula,

$$\beta F_{\text{id}}N = -\frac{5}{2} + \frac{3}{2} \ln \left( \lambda^2 \frac{\alpha}{\pi} \right). \quad (A.5)$$

For the excess free energy, the right hand side of the equation $(13)$ requires evaluating the integral

$$\mathcal{I} = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \ c(|\mathbf{r}_1 - \mathbf{r}_2|; \rho_0) \rho(\mathbf{r}_1) \rho(\mathbf{r}_2)$$

$$= \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \ c(|\mathbf{r}_1 - \mathbf{r}_2|; \rho_0) \sum_{\mathbf{R}_i} \phi(\mathbf{r}_1 - \mathbf{R}_i) \sum_{\mathbf{R}_j} \phi(\mathbf{r}_2 - \mathbf{R}_j)$$

$$= N \int d\mathbf{r}_1 \int d\mathbf{r}_2 \ c(|\mathbf{r}_1 - \mathbf{r}_2|; \rho_0) \phi(\mathbf{r}_1) \sum_{\mathbf{R}_j} \phi(\mathbf{r}_2 - \mathbf{R}_j)$$
We follow here similar steps as used in equation (A.1) for double integrals involving the product of the two \( \phi \) functions in the ideal gas part of the free energy. With substitution of \( \phi(r) = \left( \frac{\alpha}{\pi} \right)^{3/2} \exp(-\alpha r^2) \) the above expression simplifies to the form,

\[
I = N \left[ \alpha \sqrt{\frac{2\alpha}{\pi}} \int dr \ r^2 c(r; \rho_0) e^{-\frac{\alpha}{2} r^2} + 2\sqrt{2\pi\alpha} \rho_0 \int dR \ R g_s(R) \int dr \ r c(r; \rho_0) \left( e^{-\frac{\alpha}{2}(r-R)^2} - e^{-\frac{\alpha}{2}(r+R)^2} \right) \right]
\]

(A.6)

We change the variable \( R \) to \( R' \) in the integral (A.6), where \( R = \gamma_0 R' \). The second term in the last expression involving \( g_s(R) \) in equation (A.6) reduces to,

\[
2\sqrt{2\pi\alpha} \gamma_0^2 \rho_0 \int dR' \ R' g_s(R') \int dr \ r c(r; \rho_0) \left( e^{-\frac{\alpha}{2}(r-\gamma_0 R')^2} - e^{-\frac{\alpha}{2}(r+\gamma_0 R')^2} \right).
\]

(A.7)

Collecting all these results the excess part of the free energy is numerically evaluated in terms of the integral,

\[
\beta \Delta f_{\text{ex}} = \rho_0 \int dr \ c(r) \left[ 4\pi r(a_0 - a_1 e^{-\frac{\alpha}{2} r^2}) - a_2 \int \delta R g_s(\delta R) \left( e^{-\frac{\alpha}{2}(r-\gamma_0 R)^2} - e^{-\frac{\alpha}{2}(r+\gamma_0 R)^2} \right) d\delta R \right]
\]

(A.8)

where, \( a_0 = \frac{1}{\gamma_0}; a_1 = (2\rho_0)^{-1}(\alpha/(2\pi))^{3/2}; a_2 = \sqrt{2\pi\alpha} \gamma_0^2 \). The \( R \) integral is evaluated in terms of concentric shells as in the ideal gas part.

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