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# Stability of amorphous structures with voids

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Received 4 April 2001, in final form 12 June 2001

Published 2 August 2001

Online at [stacks.iop.org/JPhysCM/13/7259](http://stacks.iop.org/JPhysCM/13/7259)

## Abstract

We incorporate the role of free volume in the density function of amorphous structure and study its effects on the stability of such structures. Density functional theory is used to explore this ‘free-volume model’ of supercooled structures. Free-energy minimization is carried out using the void concentration as a variational parameter. A critical value of this concentration exists corresponding to the free-energy minima of the amorphous structure. An increase in the stability is observed due to the inclusion of voids in the density structure. This study is conducted for both weakly and highly localized amorphous structures. The free-volume concentration shows a power-law decrease with density for the weakly localized states and a linear decrease for the highly localized amorphous structures.

## 1. Introduction

The transformation of a continuum ergodic liquid into an amorphous glassy state with solid-like behaviour is an area of much current research interest. The ambiguities concerning the glassy or supercooled state have led to the development of a large number of theoretical approaches [1–4] that are used to study the basic characteristics of a system undergoing such a transition. These techniques explore both the dynamic and the thermodynamic properties of the supercooled states. A liquid is supercooled while avoiding crystallization such that its density structure loses the homogeneity of a liquid state and attains a heterogeneous density profile. From a thermodynamic point of view, the supercooled state represents a metastable state relative to the crystal and is characterized by an inhomogeneous and aperiodic density structure. This aperiodic crystal picture of the supercooled state is considered here to study its stability from a thermodynamic approach. In this work, we intend to explore the ‘free-volume’ picture of the supercooled liquid [1, 5] by studying the free-energy landscape of an amorphous lattice characterized by a finite fraction of vacancies.

Fox and Flory [6] first postulated that the liquid–glass transition resulted from the decrease of ‘free volume’ of the amorphous phase below some critical value. Subsequently, this concept was further elaborated by Cohen and Turnbull [1] and later by Cohen and Grest [5] who formally developed the theoretical aspects using percolation theory. The basic phenomenology behind

the free-volume models is that transport of particles occurs by their flow into voids of a size greater than a critical value formed by the redistribution of some 'free volume'. The latter is loosely defined as some surplus volume that is not taken up by the particles. On the basis of this theory, the relation between the free-volume concentration and the transport properties of the supercooled state like the viscosity was also investigated. Doolittle [7] found empirically that the fluidity (inverse of viscosity) of many simple hydrocarbon liquids could be represented in terms of the free volume as

$$\phi = \phi_0 \exp\left(-\frac{cv_0}{v_f}\right) \quad (1)$$

where  $\phi$  denotes the fluidity and  $c$  is a constant of order unity. Here  $v_f$  denotes the average free volume per molecule,  $v_f = \bar{v} - v_0$ ,  $\bar{v}$  being the average volume per molecule and  $v_0$  the van der Waals volume of the molecule. William *et al* [8] showed that this result is valid for a large number of glass formers. They proposed that a linear relation exists between the free volume  $v_f$  and the distance from transition on the temperature scale  $T - T_g$ . This, through equation (1), in turn gives rise to the typical Vogel–Fulcher divergence of viscosity.

The density functional theory (DFT) is an appropriate liquid-based theory to use in undertaking this study. This theory is based upon the simple idea of identifying a solid as a strongly non-uniform liquid. This notion of describing the properties of a highly non-uniform phase in terms of the fairly well-developed liquid-state theory was first put forward by Kirkwood and Monroe [9]. Later on, Ramakrishnan and Yussouff (RY) [10] formulated it in terms of the direct correlation function and successfully applied this concept to the liquid–solid coexistence problem by expressing the properties of the highly organized solid (the non-uniform phase) as a perturbation of those of the coexisting liquid. The mathematical formulation of this simple concept was further elucidated by Haymet and Oxtoby [11] and a fair amount of success has since been achieved in solving problems related to simple inhomogeneous density structures. This theory has been recently applied to study the static aspects of supercooled amorphous structures. These studies were mainly initiated by Singh *et al* [3] and were followed by similar studies using different density functional treatments [12, 13]. Two types of free-energy minimum were located for such systems. The first corresponds to highly localized amorphous structures that were identified as the 'hard-sphere-glass' state [3, 12, 13]. A different class of minima were detected [14] in the free-energy landscape of the same random structure, that represented *weakly localized* heterogeneous structures. These structures were shown to be more realistically associated with the structure of supercooled states seen in computer simulation studies. The metastable character of the different types of minimum in the free-energy landscape is explored here by modelling the 'free volume' in the density function characteristic of these structures. This has the effect of increasing the degree of heterogeneous character of the underlying amorphous structure. We compute the free-energy functional using the RY expansion around a uniform state.

The motivation of the present work is to formulate the concept of free volumes in a simple density functional formalism and use its variational nature to investigate whether there is any optimum value of the free volumes associated with the metastable phase, giving free-energy minima. In the model presented here, the free volumes in the system are constructed as the vacancies at the prescribed lattice sites of Bernal's random structure [15]. Such a modelling leads to a scenario of increased amount of local unoccupied volume in the system and that is how we define 'free volume' in this work. The major requirement of such theories is the formulation of the test density function which is relevant to the type of structure whose stability is being considered. The variational principle is then invoked to determine the density structure corresponding to the minimum of the free-energy functional. Tarazona [16] first proposed considering the ensemble-averaged density distribution as a summation over Gaussian profiles

centred over the lattice sites of the given inhomogeneous structure. Since then, such a formulation has been followed almost uniformly in all the related density functional studies. In this approach, the density is parametrized in terms of the mass localization parameter  $\alpha$  which is inversely proportional to the square of the width of the Gaussian profiles. This parameter has the effect of quantifying the motion of particles in the system. In the  $\alpha \rightarrow 0$  limit, there are Gaussian profiles of infinite width and thus the corresponding phase represents the homogeneous liquid state. Increasing values of  $\alpha$  represent increasingly localized structures, thus relating to greater inhomogeneity in the system. The  $\alpha$ -value corresponding to the free-energy minima finally determines the phase which the system prefers thermodynamically. To include vacancies in the system, the parameter space of the density function is increased. The homogeneous presence of a specific concentration of vacancies in the system leads to a uniform decrease in the number of occupied sites in each coordination shell around any arbitrary position in the system. In an ensemble-averaged picture this amounts to expressing the density function as

$$\rho(\vec{r}) = \mathcal{P} \left( \frac{\alpha}{\pi} \right)^{3/2} \sum_{i=1}^{N_L} e^{-\alpha|\vec{r}-\vec{R}_i|^2} \quad (2)$$

where  $\mathcal{P}$  actually serves as the fraction of sites present in any  $i$ th shell around the position  $\vec{r}$  in the system, such that  $\Delta_v = 1 - \mathcal{P}$  represents the vacancy concentration in the system. We assume the vacancies to be distributed homogeneously throughout the system and hence this fraction is the same for all the shells around any arbitrary position in the system. In making this approximation, we are following Jones and Mohanty [17], who considered defects in a perfect crystal structure. Here  $N_L$  is the number of lattice sites in volume  $V$  out of which  $N$  sites are occupied by the particles. The average particle density is thus  $\rho_0 = \mathcal{P}\rho_b$  where  $\rho_b$  represents the average lattice density. Thus the free-energy minimization is carried out with respect to  $\alpha$  and  $\mathcal{P}$ . These two parameters provide information on two different structural aspects of the stable phase. We mainly explore the existence of a critical free-volume concentration  $\mathcal{P}$  and its variation with density for the two different classes of minima seen for amorphous structures.

The paper is organized in the following manner. In section 2 we give the details related to the calculation of the free-energy functional formulated so as to include the effects of free volume. In section 3 we evaluate the effects on the stability of the amorphous structures caused by the inducing of vacancies in the density structure. Here we present the analysis conducted for amorphous systems in both the extremely localized and the weakly localized regimes. The implications of these results are further discussed in section 4 and the relevance for dynamical studies is explored quantitatively.

## 2. The model studied

The Helmholtz free energy can be expressed as a sum of the purely entropic contribution given by the ideal-gas term and the contribution due to the interactions in the system identified as the excess term in the general terminology:

$$\beta\mathcal{F}[\rho(\vec{r})] = \int d\vec{r} \rho(\vec{r}) (\ln(\Lambda^3 \rho(\vec{r})) - 1) - \Phi[\rho(\vec{r})]. \quad (3)$$

Here  $\rho(\vec{r})$  is the ensemble-averaged local density distribution,  $\Phi$  represents the excess part of the free energy and  $\beta^{-1} = k_B T$ .  $\Phi[\rho(\vec{r})]$  is expressed as a perturbation around  $\Phi$  for a liquid of density  $\rho_0$ . The functional Taylor series expansion in terms of the homogeneous density

distribution  $\rho_0$  is given as [10]

$$\begin{aligned} \Phi[\rho(\vec{r})] - \Phi(\rho_0) &= \int d\vec{r}_1 \delta\rho(\vec{r}_1) [-\beta\mu_0 + \ln(\Lambda^3 \rho_0)] \\ &+ \frac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 c(\vec{r}_1 - \vec{r}_2; \rho_0) \delta\rho(\vec{r}_1) \delta\rho(\vec{r}_2) \end{aligned} \quad (4)$$

where  $\mu_0$  is the chemical potential of the uniform phase and  $c(r; \rho_0)$  is the direct correlation function of the homogeneous state of density  $\rho_0$ . In the present work we consider the perturbation expansion of the excess free energy around that of the uniform system of the same density as the average density of the corresponding inhomogeneous structure, i.e.,

$$\rho_0 = \frac{1}{V} \int d\vec{r} \rho(\vec{r}). \quad (5)$$

The free-energy expression in this case reduces to the following form:

$$\beta\mathcal{F}[\rho(\vec{r})] - \beta\mathcal{F}(\rho_0) = \int d\vec{r} \rho(\vec{r}) \ln\left(\frac{\rho(\vec{r})}{\rho_0}\right) - \frac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 \delta\rho(\vec{r}_1) \delta\rho(\vec{r}_2) c(\vec{r}_1 - \vec{r}_2; \rho_0). \quad (6)$$

Here  $\delta\rho(\vec{r})$  is the deviation of the inhomogeneous state density  $\rho(\vec{r})$  from the average density  $\rho_0$ . The minimization of this free-energy functional then determines the density function corresponding to the stable (or metastable) state of the given system. The first term is the purely entropic contribution to the free energy and the interactions in the system are responsible for the second term.

This functional is then minimized in a constrained manner by specifying the underlying lattice as the input. This information is carried by the site–site correlation function  $g(R)$  of the particular structure considered. Bernal's random structure [15] is considered as a good approximation for the static structure of the undercooled liquid state. We follow the earlier approach of supplying  $g(R)$  for the Bernal structure determined from Bennett's algorithm [18] and approximate [12]

$$g(\vec{R}) = g_B \left[ R \left( \frac{\eta}{\eta_0} \right)^{1/3} \right] \quad (7)$$

where  $\eta$  denotes the average packing fraction. Here  $\eta_0$  is used as a scaling parameter for the structure [12, 13], such that at  $\eta = \eta_0$  the structure corresponds to Bernal packing, so different values of  $\eta_0$  relate to different structures. The calculations in the present work correspond to  $\eta_0 = 0.64$ . Now we elaborate on the computational aspects of reducing these expressions for the specific case of a random structure.

With the density function expressed in terms of defects, i.e. equation (2), the ideal-gas part of the free energy per particle can in general be expressed as

$$\beta \Delta f_{id}[\rho(\vec{r})] = \mathcal{P} \int d\vec{r} \phi(\vec{r}) \left[ \ln \left( \frac{\mathcal{P}}{\rho_0} \int d\vec{R} \phi(\vec{r} - \vec{R}) (\delta(\vec{R}) + \rho_0 g(\vec{R})) \right) \right] \quad (8)$$

for an amorphous structure described by the radial distribution function  $g(R)$  referred to above. This is obtained by the use of equation (2) in the ideal-gas term of equation (6). The random structure is marked by a vacancy concentration of  $\Delta_v$ . In the above expression, the function  $\phi(\vec{r} - \vec{R})$  represents a Gaussian function centred at a position  $\vec{R}$ , i.e.,

$$\phi(\vec{r} - \vec{R}) = \left( \frac{\alpha}{\pi} \right)^{3/2} e^{-\alpha|\vec{r} - \vec{R}|^2}.$$

The density structure of the system in a highly localized state is represented by sharply peaked Gaussian functions centred around the lattice sites. This asymptotic limit corresponds to large  $\alpha$  and the ideal-gas part of the free energy (equation (8)) reduces to

$$\beta \Delta f_{id}[\rho] \approx - \left[ \frac{3}{2} + \ln \rho_0 - \ln \mathcal{P} + \frac{3}{2} \ln \left( \frac{\pi}{\alpha} \right) \right]. \quad (9)$$

This is obtained by replacing the summation inside the logarithmic term by just the contribution from the nearest site. This reduction is, however, not valid for consideration of the weakly localized state of the amorphous structure where the  $\alpha$ -values are small and the Gaussian functions wide enough to cause considerable overlap over different sites, such that the above reduction can no longer be justified. Thus in the range of small  $\alpha$  we numerically evaluate equation (8) as it stands, but use equation (9) in the large- $\alpha$  regions. In our earlier work [14] we showed that these two expressions start merging for typically  $\alpha > 40$  within 1%. Similarly we formulate the evaluation of the excess term per particle as follows:

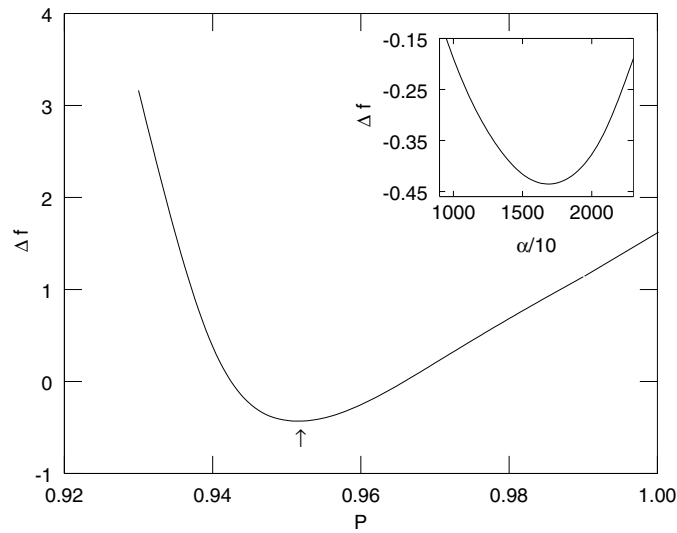
$$\begin{aligned} \beta \Delta f_{ex} = \rho_0 \int d\vec{r} c(r; \rho_0) - \frac{\mathcal{P}}{2} \int d\vec{r}_1 \int d\vec{r}_2 \phi(\vec{r}_1) \phi(\vec{r}_2) c(\vec{r}_1 - \vec{r}_2; \rho_0) \\ - \frac{\mathcal{P}}{2} \int d\vec{R} \int d\vec{r}_1 \int d\vec{r}_2 \phi(\vec{r}_1) \phi(\vec{r}_2 - \vec{R}) (\delta(\vec{R}) + \rho_0 g(\vec{R})) c(\vec{r}_1 - \vec{r}_2; \rho_0). \end{aligned} \quad (10)$$

Here the direct correlation function,  $c(r)$ , carries the liquid-state interaction information. For the description of  $c(r)$  we have used the Percus–Yevick (PY) form with Verlet–Weis correction as obtained by Henderson and Grundke [19, 20]. This concludes the formulation of the free-energy functional used to measure the effects of free volume on the stability of amorphous systems.

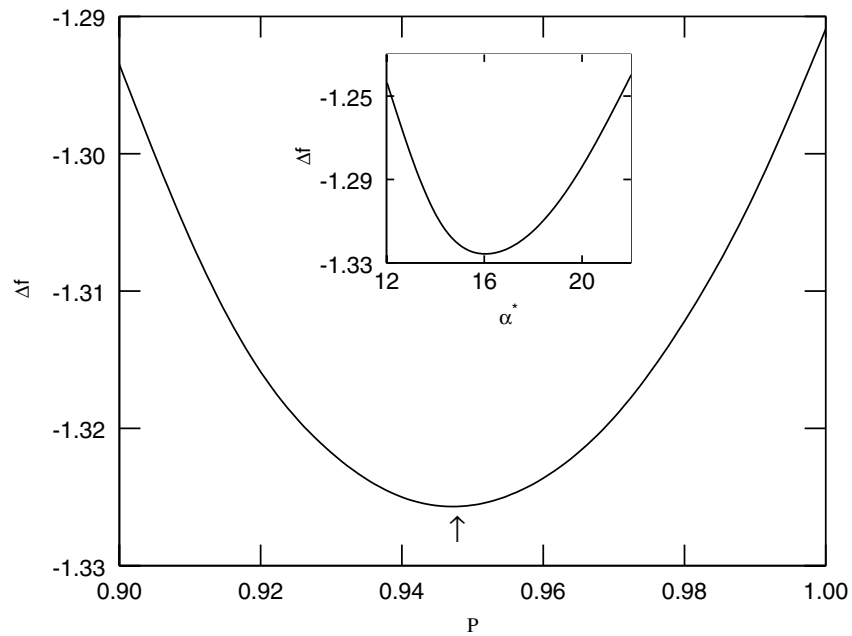
### 3. Stability of the amorphous structure

We now elaborate on the methodology used to investigate the stability of the amorphous structure characterized by a finite vacancy fraction  $\Delta_v$ . The free-energy functional is numerically evaluated using the expressions (8) to (10) at a given average density  $\rho_0^*$ , where  $\rho_0^* = \rho_0 \sigma^3$ ,  $\sigma$  being the hard-sphere diameter. The parameters  $\alpha$  and  $\mathcal{P}$  are varied simultaneously and two minima are detected in the two-dimensional  $(\alpha, \mathcal{P})$  free-energy landscape. One corresponds to the weakly localized state of the amorphous structure since it is found corresponding to low  $\alpha$ -values. The other corresponds to very highly localized structures characterized by large  $\alpha$ -values. We illustrate the minimum on the free-energy landscape with respect to the variational parameter  $\mathcal{P}$  in figure 1. Here  $\alpha^*$  corresponds to the dimensionless number  $\alpha \sigma^2$ . The values plotted correspond to the minima in the large- $\alpha$  space. The minimum value of the free energy is observed at  $\mathcal{P} = 0.951$  at density  $\rho_0^* = 1.12$ , as indicated by the arrow. This figure shows a considerable increase in the stability of the structure caused by the inducing of free volumes in the structure. The value of  $\Delta f$  decreases from 1.64 ( $\mathcal{P} = 1$ ) to  $-0.44$  due to the presence of free volume in the system. As an inset in this figure, the  $\alpha$ -space minimization is shown at the same density.

In figure 2 we show the corresponding curve for the weakly localized structure at the same density. The  $\alpha$ -space variation is shown as an inset in this figure, where each value corresponds to the vacancy concentration obtained as a partial minimum in the  $\mathcal{P}$ -space. In this case the optimum value of  $\mathcal{P}$  is obtained at 0.946, the corresponding value of  $\Delta f$  being  $-1.325$ . The effect of vacancies on the stability of the weakly localized structure is not as significant as that observed for the highly localized structures. This is because in the weakly localized structures the Gaussian profiles of the particles are already too smeared. The vacancies are not expected



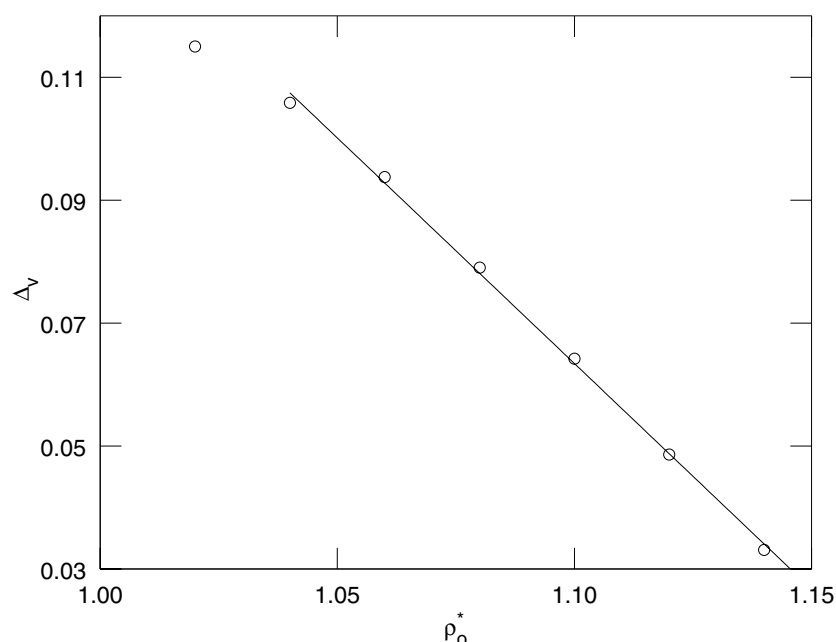
**Figure 1.** Difference in free energy per particle ( $\Delta f$ ) (in units of  $\beta^{-1}$ ) versus  $\mathcal{P}$  in the large- $\alpha$  regime ( $\rho_0^* = 1.12$ ). In the inset the corresponding minimization is shown in the  $\alpha$ -space.



**Figure 2.** Difference in free energy per particle ( $\Delta f$ ) (in units of  $\beta^{-1}$ ) versus  $\mathcal{P}$  in the low- $\alpha$  regime ( $\rho_0^* = 1.12$ ). The inset shows the variation in the  $\alpha$ -space.

to alter the density structure to a large extent and hence the free-energy values do not change by a large percentage. Nevertheless, the existence of a minimum in the  $\mathcal{P}$ -space at a value less than unity indicates the thermodynamic preference of the amorphous state for a structure characterized by a homogeneous presence of vacancies, thus establishing the ‘free-volume’ picture of supercooled states from a density functional approach.

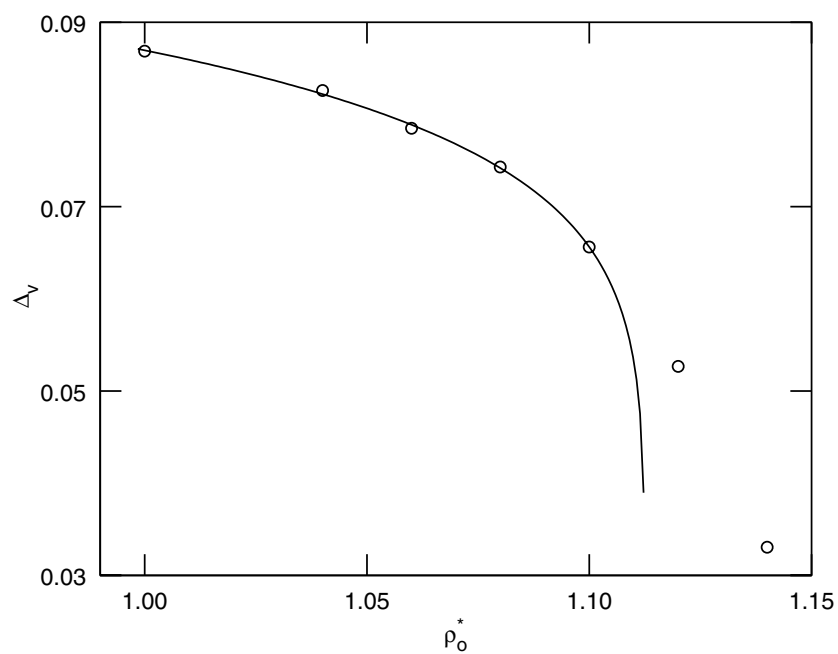
The two classes of minima observed in amorphous structures represent two different stationary states of the system and the dynamics of the system should show different characteristics around these minima. This is indicated by the two different types of behaviour shown by the variation of vacancy concentration with respect to the average density. It follows a linear relation with the average particle density of the highly localized amorphous structure. This is shown in figure 3, where the solid line is the linear curve fitting the variation of  $\mathcal{P}$  versus  $\rho_0^*$  for the state corresponding to the high- $\alpha$  minimum. This predicts that the system will completely freeze, i.e., the free-volume concentration will vanish, at packing fraction  $\eta = 0.62$ . Figure 4 illustrates the corresponding curve for the weakly localized structure, corresponding to the lower values of the width parameter. In the lower- and intermediate-density regions, the free-volume concentration shows a power-law decrease with the increase in the density. The solid curve shows this functional variation that shows the divergence at  $\eta = 0.58$  with an exponent 0.128.



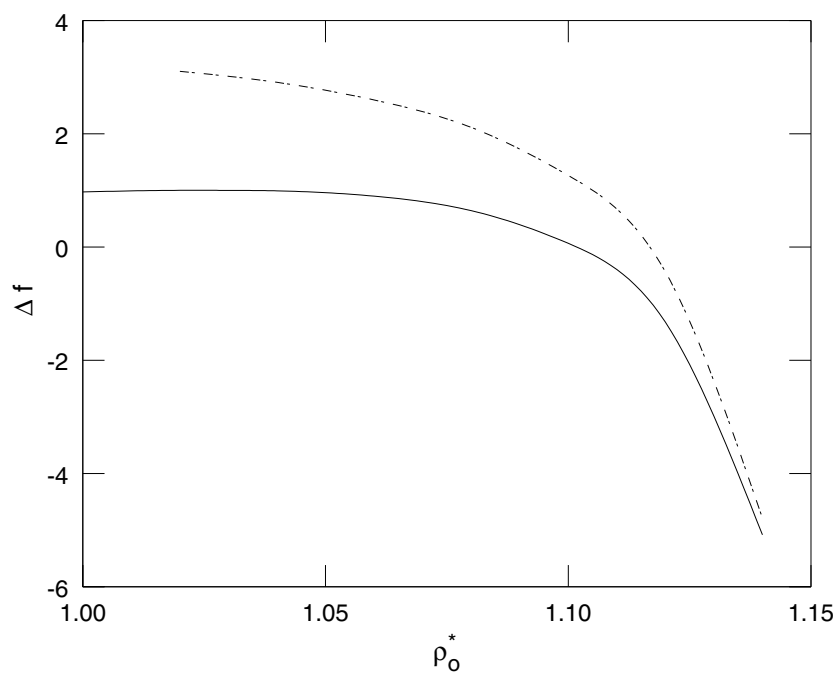
**Figure 3.** Free-volume concentration ( $\Delta_v$ ) versus density  $\rho_0^*$  for the highly localized amorphous structure. The solid line shows the linear fit.

In figure 5 we have shown the variation of the free energy versus the average density for both the highly localized and the weakly localized amorphous structures. The metastability of the highly localized amorphous structure starts coming close to that of the weakly localized state at higher densities due to the inducing of free volumes in the structure. The highly localized state starts becoming more stable than the homogeneous state after density  $\rho_0^* = 1.12$ . For the similar density structures considered without defects, this density has been reported to be 1.14 [3]. Figure 6 illustrates the value of the width parameter  $\alpha$  that minimizes the free-energy difference in a weakly localized amorphous structure with a *fixed* defect concentration at density  $\rho_0^* = 1.08$ . This figure shows the partial minimization of the free energy with respect to the width parameter  $\alpha$  and not complete minimization. It demonstrates the fact that with a smaller concentration of free volume (larger  $\mathcal{P}$ ), a more localized structure (larger  $\alpha$ ) results. This basically highlights the competition between the configurational and the interaction parts

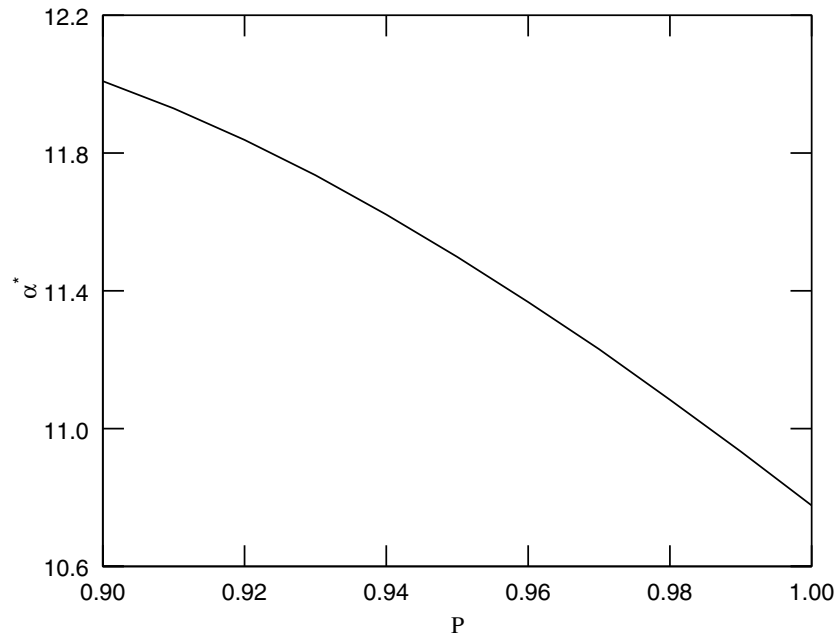




**Figure 4.** Free-volume concentration ( $\Delta v$ ) versus density  $\rho_0^*$  for the weakly localized amorphous structure. The solid line shows the power-law fit.



**Figure 5.** Difference in free energy per particle ( $\Delta f$ ) (in units of  $\beta^{-1}$ ) versus  $\rho_0^*$ . The solid line corresponds to the small- $\alpha$  free-energy minimum and the dashed line corresponds to the highly localized structure.



**Figure 6.** The variation of the  $\alpha$ -minimum with the corresponding value  $\mathcal{P}$  at density  $\rho_0^* = 1.08$ .

of the free energy at different  $\mathcal{P}$ -values which forces the metastable structure to take on a higher level of localization with the increase in free volumes.

#### 4. Discussion

We have investigated various features of the supercooled states by considering the presence of a finite void concentration in an amorphous lattice. In formulating the test density function of the amorphous structure we have extended the idea used by Jones and Mohanty [17], who considered defects in crystal structures using a modified density function. The role of free volumes in amorphous states is already known from earlier works [5, 6]—in the present work we study this on the basis of a density functional approach. The parameter  $\mathcal{P}$  is introduced which measures the concentration of occupied sites in the lattice and thus marks the presence of free volumes in the structure. The existence of the free-energy minima with respect to  $\mathcal{P}$  demonstrates the thermodynamic preference of the amorphous state for a particular concentration of free volume corresponding to a specific density. That this brings about a decrease in the free energy of the structure shows that the metastability of the supercooled states is dependent upon the concentration of ‘free volume’ present in the structure.

We employ this definition of ‘free-volume’ density distribution in the context of both types of amorphous structure observed at a given density. The two structures differ with regard to the level of mass localization specific to each of these minima. This can be identified from the value of the width parameter  $\alpha$  specific to these structures. The parameter  $\alpha$  measures the average width of the Gaussian profile characterizing the density distribution in the supercooled state. For the value of  $\alpha^* \approx 16$  corresponding to the free-energy minimum at  $\rho^* = 1.12$  (in figure 2), this width ( $d = 1/\sqrt{\alpha}$ ) is  $\approx 0.25 \sigma$ , which is about triple the corresponding value for the crystal density function. This value relates to the situation in between the two limits

and can be associated neither with the liquid density profile ( $\alpha \rightarrow 0$ ), nor with the extremely localized case of a crystal. Computer simulation results of LaViolette and Stillinger [21,22] also produced values of the root mean square displacement in the supercooled states similar to those indicated by  $\alpha$  corresponding to the free-energy minimum in our work [14]. The supercooled state is marked by the particles having a more restricted motion as compared to a normal liquid. A highly localized heterogeneous structure in the amorphous state was first predicted by Singh *et al* [3]—called the hard-sphere glass. Subsequently, the new class of minima [14] that shows up as a result of random packing was found. It signifies metastable states (w.r.t. the crystal state) distinct from the homogeneous liquid state. The use of the parameter  $\mathcal{P}$  in the present context, allowing the total number of sites to be higher than the number of particles, is introduced to model the presence of voids or free volumes in the amorphous structures. It is in this spirit that we *do not* restrict our theory to just the highly localized or small-width-density distribution (large  $\alpha$ ). The consideration of the small- $\alpha$  minimum thus models loose structures with voids. It should be noted that the fraction of free volume is much larger here as compared to the case for vacancies in the crystal.

We observe that the weakly localized states which correspond to the free-energy minimum found in the region of small width parameter of the Gaussian density profiles are less affected by the presence of free volumes. Thus the free energy does not change much although a clear minimum is observed with respect to the defect parameter  $\mathcal{P}$  at a non-zero value of  $\Delta_v$ . On the other hand, at higher densities the stability of the highly localized states comes closer to that of the weakly localized states, thus demonstrating that at higher densities the supercooled state is likely to be characterized by the more localized density structures. However, we would like to mention here that for the ‘hard-sphere-glass’ state, the structures do correspond to very large values of the width parameter  $\alpha$  in this theory and similar results were also reported by Singh *et al* [3]. This is peculiar to the use of the RY functional form for the free-energy functional. In the large- $\alpha$  region where the density distribution is highly localized, the truncation of the density functional expansion at second order is not a very good approximation. In the case of the more delocalized structures, the corresponding value of the width parameter is low and the above truncation is more applicable. We have not used any non-perturbative formulation of the theory, since most such formulations globally map the inhomogeneous structure into an ‘equivalent’ liquid satisfying certain criteria [23]. Following the signatures of subtle inhomogeneous effects like the presence of a small percentage of vacancies is thus unlikely to be achievable. Thus for qualitative investigation purposes, our use of the RY functional approach is well justified in this study.

We would also like to stress here that the major criticism of the results of the similar calculation done for the crystal structure in [17] arises from the fact that it predicted large values of  $\Delta_v$ . These were not in accord with the experimental findings, which predicted the defect densities in the crystal to be less by at least two orders of magnitude than that predicted by Jones and Mohanty. In the present study, although we have used the mathematical formulation of the density function, the physical interpretation is entirely different. The defects in this study are a measure of the average amount of unoccupied volume present in the amorphous structure. The concentration is actually indicative of liquid-like behaviour or ease of mass transport in the supercooled state. The vanishing of this free-volume concentration is interpreted as a complete freezing of motion in the system and hence the relevance of this concept is not undermined by the critical value of  $\Delta_v$  obtained.

Since the free-volume concentration is a measure of the transport properties in a system, qualitative conclusions can also be drawn as regards the dynamical aspects. This study indicates that the decrease of the free volume can in general be associated with increase in viscosity of the system. Knowledge of the variation of the free volume with density/temperature is useful in

extracting the temperature dependence of the transport coefficients. We observe two different types of behaviour for the two different free-energy minima. The highly localized structures display a linear decrease in the free-volume concentration with the increase in density. On the other hand, the weakly localized structures, characterized by low values of the width parameter, show a power-law decrease in the free-volume concentration with respect to density. It is well known that a large number of laboratory systems and computer simulations of simple systems show a weak power-law-type divergence of viscosity with decrease in temperature—approaching the mode-coupling instability generally denoted by  $T_c$ .  $T_c$  is a temperature higher than the calorimetric glass transition temperature  $T_g$  at which all mass transport practically freezes. Such dynamical theories consider fluctuations around a disordered liquid state and the role of their dynamic coupling. Thus this result suggests that the low- $\alpha$  free-energy minima may correspond to the stationary state around which the fluctuations are considered in the dynamical studies coming within the realm of mode-coupling theories [24]. However, this would require further investigation and a definite relation to be established between the free-volume concentration and the transport properties.

### Acknowledgments

SPD acknowledges the support from grant INT9615212 from NSF. CK acknowledges financial support from the University Grants Commission (UGC) of India.

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