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On the Free-Volume Model of the Liquid-Glass Transition*

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We have improved the free-volume model for molecular transport in dense fluids, as developed in earlier papers, by taking account of the variable magnitude of the diffusive displacement. The development is carried through in a way which may display more clearly the relation between the free-volume model and the Enskog theory. Implicit in the free-volume development is the association, on the average, of a correlation factor $f(a)$ with each magnitude, a , of the displacement. It is assumed that $f(a)$ is a step function which is zero, because of the predominance of back scattering, for $a < a^*$ and unity for $a > a^*$. This corresponds to dividing the displacements sharply into two categories, one "gaslike" and the other "solidlike." Molecular dynamics computations have shown that the self-diffusion coefficient in the hard-sphere fluid at the highest densities is falling precipitously, with increasing density, away from the Enskog values. It appears that this density trend, which was attributed to back scattering, if continued, would lead to a continuous solidification. It is shown that the magnitude and density trend of this deviation are described satisfactorily by the free-volume expression, where the free volume is referred to the specific volume of the Bernal glass. We conclude that at least the molecular transport manifestation of a liquid-glass transition can be deduced entirely within the framework of the van der Waals physical model for liquids with due corrections for the variation of the effective hard-core radius with temperature. The free-volume model results from a crude, but physically plausible, approach to this problem.

INTRODUCTION

We^{1,2} and others³⁻⁶ have developed a simple free-volume model to account for diffusive transport in liquids and glasses and for the liquid \leftrightarrow glass transition. This model was developed originally for a dense hard-sphere fluid, in which the free volume is well defined, and then applied to the interpretation of transport and glass transition behavior in simple molecular systems.

An important deduction from the model is a crude correction for the effects of back scattering, neglected in the Enskog theory, on diffusive transport. According to the model, diffusive motion will be canceled by back scattering in those parts of the system which are locally most dense. This means that at a sufficiently high average density virtually all the molecular motion become redundant, owing to back scattering, and the transport behavior approaches that of a solid. Whatever other features a satisfactory model for the liquid \leftrightarrow glass transition may have, it seems that it must account for a transition from the Enskoglike to the solidlike regime in back scattering behavior.

Recently, results on the rate of self-diffusion in dense hard-sphere fluids have become available from molecular dynamics studies.⁷ The measured rates are in good agreement with the Enskog theory at the lower densities but fall significantly below the predictions of the theory at the highest fluid densities.

In this paper we present a rederivation and improvement of the free-volume model which, we hope, will make its physical basis and its relation to the Enskog theory more clear. Also we discuss the interpretation of the molecular dynamics results and the possibility of a fluid \leftrightarrow glass transition in a hard-sphere system in terms of the model.

MODEL AND ANALYSIS

In terms of the distance a traveled by the particle between collisions, the self-diffusion coefficient, D , in a hard-sphere system may be expressed as

$$D = \frac{1}{3} \bar{u} \bar{f} \int_0^{\infty} p(a) a da, \quad (1)$$

where $p(a)$ is the probability that the displacement, a , lies between a and $a+da$ and \bar{u} is the average gas kinetic velocity. \bar{f} is the correlation factor which is unity for a random walk; it should, indeed, be unity, as Enskog assumed, in the fluid at sufficiently low density but it ought to approach zero in the perfect crystal or ideal glass at high density.

A concept implicit in our free-volume model is that, on the average, a correlation factor $f(a)$ may be associated with each magnitude of the displacement. This comes from our assumption that a is on the average some function, $a(v)$, of the free volume, v , of the cage (Voronoi polyhedron), delineated by the immediate neighbors of the moving particle. Then:

$$\bar{f} = \frac{\int_0^{\infty} p(a) f(a) a da}{\int_0^{\infty} p(a) a da} \quad (2a)$$

and

$$D = \frac{1}{3} \bar{u} \int_0^{\infty} p(a) f(a) a da. \quad (2b)$$

At a sufficiently high average density we expect that $f(a) \rightarrow 0$ as $a \rightarrow 0$ and $f(a) \rightarrow 1$ as $a \rightarrow \infty$.

If a is, on the average, a function of the free volume of the cage, the self-diffusion coefficient may be put in

the alternative form

$$D = \frac{1}{3} \bar{u} \int_0^{\infty} p(v) f(v) a(v) dv, \quad (3)$$

where $p(v)$ is, as in the earlier paper, the probability that the free volume of the cage lies between v and $v+dv$ and $f(v)$ is the correlation factor for displacements within a cage in which the free volume is v . We showed that for the most probable distribution of the total free volume,

$$p(v) = (\gamma/v_f) \exp(-\gamma v/v_f), \quad (4)$$

where v_f is the average free volume ($=\gamma \sum N_i v_i / \sum N_i$) per cage and γ is a numerical factor between $\frac{1}{2}$ and unity to correct for overlap.

$f(v)$ must go from 0 at $v=0$ to 1 at $v=\infty$. Our basic assumption was that $f(v)$ is a step function such that it is zero for $v < v^*$ and unity for $v > v^*$ and that v^* is independent of the average density of the system. The step-function assumption would be a fair approximation if the form of $f(v)$ is sigmoidal as represented schematically in Fig. 1. It corresponds to dividing the displacements sharply into two categories, one "gas-like" and the other "solidlike", as has been proposed in some interpretations of the scattering of low energy neutrons by real liquids.⁸

In our earlier paper we arbitrarily set $a(v)$ equal to a constant, $a_0/2$, where a_0 is the sphere diameter, for all $v > v^*$. It seems more reasonable to approximate $a(v)$ by the linear relation

$$a(v) = \alpha v, \quad (5)$$

which would be strictly valid only in the limit $v \rightarrow 0$. With the foregoing assumptions and substituting $p(v)$ from Eq. (4) into (3) we obtain

$$D = \frac{1}{3} \frac{\bar{u}\gamma}{v_f} \int_{v^*}^{\infty} \alpha v \exp\left(\frac{-\gamma v}{v_f}\right) dv \quad (6)$$

and upon integration

$$D = \frac{1}{3} (\bar{u}\alpha) [v^* + (v_f/\gamma)] \exp(-\gamma v^*/v_f). \quad (7)$$

This takes the form, $D = (\bar{u}\alpha v^*/3) \exp(-\gamma v^*/v_f)$, of our earlier expression when $v^* \gg v_f/\gamma$ and reduces to: $D = (\bar{u}/3) (\alpha/\gamma) v_f$ when $v_f/\gamma \gg v^*$. The average correlation factor is obtained by dividing Eq. (7) by $\bar{u}\alpha v_f/3\gamma$; it is

$$\bar{f} = [1 + (\gamma v^*/v_f)] \exp(-\gamma v^*/v_f). \quad (8)$$

If, as we have supposed, the displacements scale as the cage free volumes, v , the form which we have obtained for $p(v)$ should be the same as that of the distribution function, $p(a)$, for the displacements. In fact, theory predicts that $p(a)$ should fall exponentially and this was confirmed by the results of molecular dynamics computations.⁹ That is,

$$p(a) = (1/\lambda) \exp(-a/\lambda), \quad (9)$$

which is equivalent, in form, to Eq. (4). Also if $f(a)$

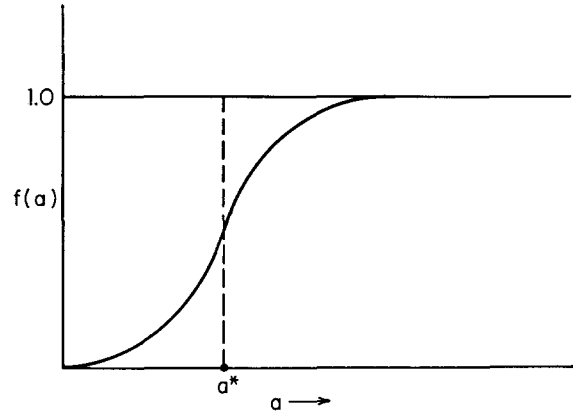


FIG. 1. Possible sigmoidal form of $f(a)$ and the step-function approximation to it.

has the form assumed for $f(v)$, that is, $f(a) = 0$ for $a < a^*$ and $f(a) = 1$ for $a > a^*$, we may formulate D in terms of the displacements as follows:

$$D = \frac{\bar{u}}{3\lambda} \int_{a^*}^{\infty} a \exp\left(-\frac{\lambda}{a}\right) da. \quad (10)$$

This leads to

$$D = \frac{1}{3} (\bar{u}\lambda) [1 + (a^*/\lambda)] \exp(-a^*/\lambda), \quad (11)$$

and

$$\bar{f} = (1 + a^*/\lambda) \exp(-a^*/\lambda), \quad (12)$$

which are analogous to Eqs. (7) and (8). Thus when the displacement is related linearly to the local free volume, as it may be in the high density regime, the formulation of D in terms of free volume seems entirely equivalent to its formulation in terms of the displacements, with v_f analogous to λ and v^* analogous to a^* .

DISCUSSION

With an exponential distribution of displacements the major contribution to the self-diffusion coefficient in the hard-sphere fluid would come from the larger displacements, even if \bar{f} were unity. For example, roughly $\frac{2}{3}$ of the magnitude of D would be contributed by the $\frac{1}{3}$ of the displacements which are largest. Thus according to our step function model for $f(v)$, decreasing \bar{f} below unity by a small fraction would require that a much larger fraction of the displacements be rendered non-diffusive by back scattering.

Alder and Wainwright⁷ have determined the self-diffusion coefficient in a three-dimensional hard-sphere system from molecular dynamics computations. They found that \bar{f} rises with increasing density to a maximum of 1.16 at a density (\bar{v} and v_0 are the average volumes per particle in the fluid and ideally close-packed crystal, respectively) v_0/\bar{v} , $\frac{1}{3}$ of that at close packing¹⁰; the substantial positive departure of \bar{f} from unity was later associated with motions due to vortices.¹¹ With further increase in density, \bar{f} falls precipitously and is 0.49 at the highest density, $v_0/\bar{v} = 0.67$, which is very near the

density at the thermodynamic crystallization pressure, for which measurements have been obtained.¹² The sharp falling off of \bar{f} with increasing density beyond the maximum was attributed⁷ to the onset of back-scattering effects. \bar{f} would approach zero rather quickly, corresponding to a continuous solidification, if its trend with density continued.

Interpreting these results in terms of the free-volume model, about 80% of the displacements would be non-diffusive at the density $v_0/\bar{v}=0.62$ ($\bar{f}=0.68$) if we attribute the entire decrease of \bar{f} from its maximum to back scattering. To see if the free-volume model is consistent with the results it is necessary to make some choice, v_0' , for the specific volume of the state to which the average free volume, $v_f = \bar{v} - v_0'$, is referred. This state might be a crystallite assembly reached continuously or a random assembly of spheres of the type studied by Bernal and associates.¹³ We have suggested¹⁴ that the dense random structure of Bernal, which has a density roughly 0.85 of that of ideal crystalline packing, models an amorphous solid in internal equilibrium ("ideal glass"). If this is the state approached continuously by the fluid when it is compressed, we would expect that v_0' would be larger than or equal to the specific volume of the dense random structure, $1.17v_0$. Setting v_0' equal to this limiting value we find that the magnitude and density trend of the modified average correlation factor, $\bar{f}' = \bar{f}/f_{\text{max}} = \bar{f}/1.16$, at the highest density are described satisfactorily by

$$\bar{f}' = [1 + (0.62v_0)/(\bar{v} - 1.17v_0)] \exp[-0.62v_0/(\bar{v} - 1.17v_0)]. \quad (13)$$

In particular, the comparison between the molecular dynamics (MD) and calculated \bar{f}' are: at $v_0/\bar{v}=0.67$, $\bar{f}'_{\text{MD}}=0.43$, $\bar{f}'_{\text{calc}}=0.435$; at $v_0/\bar{v}=0.62$, $\bar{f}'_{\text{MD}}=0.58$, $\bar{f}'_{\text{calc}}=0.58$; at $v_0/\bar{v}=0.56$, $\bar{f}'_{\text{MD}}=0.81$, $\bar{f}'_{\text{calc}}=0.74$. This fit may not be highly significant since so few results are available for the high density regime where the model should be most applicable. Also we have ignored the apparent increase, beyond the maximum \bar{f} , in the correction factor, f_v , for motions due to vortices. However, the hard-sphere results do indicate that, consistent with the physical assumptions of the free-volume model, the back-scattering correction is significant and increasing sharply with density at densities near to but less than the fluid density, v_0/v_m , at the thermodynamic crystallization pressure. This trend suggests that \bar{f} would, indeed, fall to very small values, corresponding to a continuous solidification at densities approaching v_0/v_0' .

The free-volume model may be applicable to the interpretation of molecular transport behavior in those actual liquids which behave according to the van der Waals physical model. While the van der Waals model describes the high temperature behavior of simple dense fluids fairly well, it can be improved somewhat by taking account of the "softness" of the cores of actual

molecules. One effect of this softness can be described by a decreasing "effective" hard-core diameter, d_{eff} , with increasing temperature. Using d_{eff} values deduced from equilibrium data, Dymond and Alder¹⁵ showed that the transport behavior in dense fluid argon at high temperature is in fair accord with the Enskog theory. Another effect of core softness, demonstrated by Naghizadeh,³ is that the energy required to redistribute the free volume, which is taken to be zero in the simple model,^{1,2} can be substantial in the lower temperature range. By taking account of this redistribution energy, Naghizadeh found good agreement of the pressure and temperature dependence of the self-diffusion coefficients of the rare-gas liquids with the free-volume model. Both effects of core softness can be important when the pressure dependence of transport rates is interpreted in terms of the free-volume model.

When the free-volume model is applied in its simplest form, the value of v_0' giving the best fit to the experimental data is chosen. If the free volume varies linearly with temperature, this is equivalent to specifying the constant T_0 in the Fulcher¹⁶ equation,

$$\tau = A \exp[b/(T - T_0)],$$

which is known to describe satisfactorily the isobaric temperature variation of the time constants, τ , for molecular transport or relaxation from the high temperature regime into, but not entirely through, the temperature regime in which the glass transition occurs. The best-fitting values for v_0' and T_0 usually prove to be quite near the specific volume and temperature, respectively, of the system at the glass transition point as usually defined.

In our earlier paper¹ we showed that the experimental molecular transport behavior of certain simple liquids is described satisfactorily by a limiting form, in particular: $D = (\bar{u}\alpha v^*/3) \exp(-\gamma v^*/v_f)$, of the free-volume Eq. (7) derived here. In these comparisons we arbitrarily set αv^* equal to $a_0/2$. In the displacement formulation, Eq. (11), this is equivalent to setting $a^* = a_0/2$ and supposing that the mean-free path, λ , is negligible in comparison with a^* . In the hard-sphere system at densities approaching v_0/v_m , λ is found to be of the order $a_0/15$ to $a_0/20$. For example, at the density $v_0/\bar{v}=0.62$, $\lambda \sim a_0/17$, and we fit the hard-sphere data with $a^* \sim 1.5a_0/17$. The vortex correction factor f_v also must be taken into account and, from rough extrapolation of Alder's results, it would be of the order of 1.5 at this density. Therefore, the factor which is to be compared with $a_0/2$ in our earlier interpretation of the data is $f_v(\lambda + a^*)$, which is $\sim 3.7a_0/17$ or $a_0/4$ to $a_0/5$ at the density $v_0/\bar{v}=0.62$. In any detailed test of the model the possibility would also have to be considered that the correlation factors $f(a)$ associated with the very long displacements are substantially larger than unity. That this is a possibility is indicated by the finding of Bennett and Alder¹⁷ that during the *traverse* of a sphere into a neighboring vacancy, in a three-

dimensional hard-sphere crystal, the moving sphere is scattered on the average about 3 times by glancing collisions. Actually, the vortex correction factor might be best ascribed to correlation factors larger than unity. However, for testing the present state of the model it seems appropriate to include it in the pre-exponential factor.

Perhaps a more significant and better fit of the experimental results on simple liquids to the free-volume model would be achieved by taking account of the variation of the pre-exponential factor in Eqs. (7) and (11) with average free volume. However, this correction would be at least partially offset by the growth of the vortex motion correction with density and possibly by an enhancement of $f(a)$ for the long displacements. What is most significant is that the major trends of the molecular transport behavior, especially the rapid increase in the time constant for molecular motion as the glass transition is approached, are predicted satisfactorily by the model.

The free-volume equation which fits the high temperature transport data overestimates the time constant, τ , for molecular transport and relaxation when the viscosity exceeds $\sim 10^7$ P. At the glass transition temperature the disparity is quite large. Actually, the Williams, Landel, and Ferry (WLF) equation¹⁸ which has been used to fit the molecular transport behavior through the glass transition has the same form as the Fulcher equation but the constants required for this low temperature regime are quite different in magnitude from those for the higher temperature regime. Recently, it has been reported¹⁹ that the viscosity-temperature relation of some simple molecular glass forming liquids at $\eta \geq 10^6$ are better described by an Arrhenius than by the WLF relation. These results suggest that after \bar{f} has fallen to very low values, a different flow mechanism becomes predominant.

For systems in which molecular transport is limited by a potential barrier, Adam and Gibbs²⁰ developed a model which led to a relation between the time constant, τ , for the transport and the configurational entropy, S_c , as follows:

$$\tau = A \exp(b/TS_c).$$

S_c is the difference in entropy between the liquid and an ideal glass; it is taken to be 0 at a temperature T_0 which appears to be near the corresponding constant in the WLF equation for the low temperature flow regime. In some systems v_f and S_c , when small, may be linearly related²¹ so that the free volume and configurational entropy formulations would, for these cases, be equivalent.²²

Near the glass transition the molecular transport rate

in most materials may be limited by potential energy barriers due to the large energy which may be required for redistributing the free volume.^{2,3} However, it appears that the rapid falling away of the transport rate from the Enskog values as the glass transition is approached is understandable within the framework of the van der Waals model by taking due account of the onset of the back-scattering correction. The free volume model in its simplest form represents a crude approach to this problem which nevertheless has physical plausibility and analytical simplicity.

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