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A molecular explanation of the transition from viscous to hopping mechanism of mass transport in the supercooled liquid near the glass transition

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When the viscosity of a supercooled liquid becomes large, the mechanism of mass transport is known to undergo a change from viscosity dependent, Stokes–Einstein behavior to an activated hopping dominated, almost viscosity independent behavior. This change is known to occur rather sharply near the temperature T_c where the mode coupling theory predicts singularities in the transport properties of the liquid. However, the origin of this change in the transport mechanism is not well-understood. Here we suggest a simple microscopic interpretation of this crossover. Our analysis is based on a scaled particle theory calculation of the activation energy for hopping and the non-Markovian rate theory of activated barrier crossing. We find that as the liquid is progressively supercooled, the activation barrier for hopping increases rapidly which makes the curvature at the barrier top also to increase. At high densities the latter gives almost a viscosity independent hopping rate which becomes more dominant at large viscosities where the collective diffusion becomes inefficient. The suddenness of the crossover is because as the density is increased, the hopping rate also decreases rapidly because of the increase in the activation energy, and a rapid increase in viscosity is required to tilt the balance in favor of the hopping mechanism. The latter can only happen at a dynamic singularity where the viscosity undergoes a sharp increase. The present analysis also offers an explanation of the decoupling of structural relaxation from the viscosity at large values of latter—such a decoupling has been suggested recently by Angell. Our analysis also provides a tentative explanation of the recent simulation results of Keyes and co-workers. © *1994 American Institute of Physics.*

I. INTRODUCTION

When a liquid is cooled very fast, the transition to the crystalline solid can often be avoided and the system can be found in the supercooled, metastable state. At small degree of supercooling the properties of the liquid are not drastically different from those expected of an equilibrium liquid, had it existed at that temperature and density. However, as the degree of supercooling becomes large, several interesting behavior emerges, such as the power-law dependence of the self-diffusion coefficient and the viscosity of the liquid on the temperature. These phenomena have been treated recently within the framework of the powerful mode-coupling theory[1] which seems to explain fairly well the dynamics of a supercooled liquid until the viscosity becomes large (about 10–100 P). In its initial formulation, the mode coupling theory predicted a dynamic transition at a critical temperature T_{MC} substantially above the glass transition temperature. Beyond this temperature, several additional new features appear in experiments which are still not well understood and which are not explained by the simple mode-coupling theory. For example, if the rise in viscosity is still fitted to a power law, often a very large exponent (in the range of 6–24) is obtained.[2] Another interesting result is the apparent crossover of diffusion from the viscous mechanism of mass transport to a hopping mechanism,[1,3] with a concurrent break-

down of the Stokes–Einstein relation between diffusion and viscosity. This crossover seems to happen rather sharply near T_{MC}. After the crossover the diffusion coefficient shows an Arrhenius temperature dependence indicating the occurrence of transport by an activated hopping mechanism. This change of mechanism of transport has sometimes been attributed to the breakdown of ergodicity of the system. Thus, a typical supercooled liquid has two regimes of viscous or diffusive behavior, separated by a temperature, T_C which seems to be close to T_{MC}. At temperatures above T_C, the behavior is nearly universal, as predicted by the mode-coupling theory while at temperatures below T_C, the dependence of the diffusion coefficient on inverse temperature is exponential.

In view of the above facts, one may ask the following questions:

(1) Why does the crossover occur sharply near a temperature that is predicted for the dynamic transition by the mode-coupling theory? As stated earlier, at this temperature viscosity is typically in the range 10–100 P which is much larger than the viscosity of an ordinary liquid near melting point which is only a few centipoise.

(2) How does the activated hopping itself survive at such high viscosities? This is somewhat paradoxical because a dense supercooled liquid is in the overdamped limit of momentum relaxation. Therefore, the rate of an activated process may be given by the Smoluchowski limit of Kramers' theory[4] which is given by the following expression:

$$k_{SL} = \frac{\omega_R \omega_b}{2\pi\zeta} \exp(-E_{act}/k_B T), \qquad (1)$$

where ω_R and ω_b are the harmonic frequencies of the ground and the activated states, E_{act} is the activation energy, ζ is the friction coefficient proportional to the viscosity, k_B is Boltzmann constant, and T is the temperature. Therefore, the hopping rate of activated barrier crossing should also decrease as inverse viscosity in this regime.

To the best of our knowledge satisfactory answers to the above questions are not yet available. In the recent extensions of the mode coupling theory,[5] the crossover to the hopping behavior is explained by introducing a coupling between the number density and the transverse current density. This extension appears to be successful in explaining the crossover, although some residual difficulties remain, as pointed out recently by Kawasaki.[6] In particular, the parameter that gives the measure of the importance of the activated process needs to be adjusted at each temperature and the usefulness of the mode-coupling theory is questioned when the activated processes become so important as to mask the MCT bifurcation singularity.[6] In addition, the extended mode-coupling theory seems to be not fully satisfactory in providing a simple physical picture of the crossover.

In this connection we should point out the interesting observations made by Seeley, Keyes, and Madan.[7] These authors calculated the diffusion coefficient by using the normal harmonic modes of a low temperature liquid. These authors found that the diffusion coefficient correlates rather well with the low frequency limit of Kramers' theory while the Smoluchowski rate expression provides a satisfactory explanation only in the supercooled liquid above the glass transition temperature. Seeley et al. considered this as a surprising result.

In this article we present a simple scenario of mass transport which may help in explaining some aspect of this dynamic transition. Our explanation is based on the observation that as the viscosity becomes very large, the rate of transport by hopping gets decoupled from viscosity by a mechanism suggested by the Grote–Hynes theory[8] of the rate of non-Markovian barrier crossing. An important ingredient of this work is an explicit calculation of this hopping rate and the calculation of the hopping diffusivity. In order to calculate the hopping rate we need to calculate the activation barrier which is obtained by using the scaled particle theory of Reiss and co-workers.[9] We also need to obtain the frequency dependent friction coefficient. This is obtained by two independent methods. First, we use the mode coupling theory[1,10] to obtain the frequency dependent friction. Second, we use the generalized hydrodynamic model of Zwanzig and Bixon.[11]

The important physical mechanism of dynamical transition that emerges from this study is the following. At small supercooling when the viscosity is relatively small, the viscous mechanism is much more efficient than the hopping mechanism. As the temperature is cooled towards the mode-coupling transition temperature, not only the viscosity increases sharply, but the barrier frequency also increases. When the viscosity suddenly becomes very large near the mode coupling transition temperature, the viscous mechanism of mass transport becomes ineffective. At this point

hopping diffusion becomes decoupled from the macroscopic viscosity because a high barrier hopping probes primarily the high frequency components of the solvent response. When the liquid is supercooled the viscosity becomes large because density relaxation becomes increasingly slow. Thus, the low frequency part of the relaxation spectrum becomes increasingly populated while the high frequency part gets less affected. That is, the spectrum becomes bimodal. Since the hopping is coupled essentially to the high frequency relaxations, it gets decoupled from the low frequency motions that contribute to the viscosity. However, for the observed crossover to occur, the viscosity must become sufficiently large to make the diffusive mechanism less significant than the hopping mechanism. For a typical liquid this seems to happen in the range 10–100 P. In the present calculations, however, a larger increase is required, as discussed below.

We should caution the reader at the outset that we are neither proposing a theory of glass transition nor a theory to calculate the self-diffusion coefficient—this communication is restricted only to providing a probable interpretation for the change of diffusive mechanism. In fact, this work may be viewed as an attempt to provide a physical and quantitative interpretation of one part of the hierarchial decoupling of relaxation proposed by Angell in the recent past.[12] In this mechanism, it was proposed that as the glass transition is reached, different modes of relaxation (for example, mechanical and transport) become decoupled from each other. To the best of our knowledge, there, however, do not exist any quantitative theory of this rather elegant scheme.

The theoretical discussions presented here differ from the previous discussions in terms of system free energy minima and barriers which are often used to describe relaxation in glasses and supercooled liquids. The latter discussions became popular after Stillinger and Weber[13] showed that a liquid can be characterized by its "inherent structures" which can be obtained by quenching the liquid. These inherent structures are characterized by local minima of the total energy of the system and are separated from each other by free energy barriers. Relaxations occur by transitions between such free energy minima.[13,14] The difficulty of this scheme is that it is not straightforward to relate these transitions (which are between minima of the whole system) to single particle diffusion which is measured in experiments. Following an approach pioneered by Zwanzig,[15] Madan, Keyes, and Seeley[16,7] have carried out extensive computer simulations to identify the barrier heights and the barrier curvatures and also calculate the diffusion constants across the glass transition temperature. While the simulations found the usual rapid decrease of the diffusion constant as the glass transition temperature is approached, it also revealed that a small, several orders of magnitude smaller than the normal liquid state value, diffusion coefficient persists in the "glassy state." The interesting observation is that while the diffusion in the liquid side could be described by the overdamped, Smoluchowski-type description of the rate of transitions over the barriers, a simple transition state rate description provides even a better description of the same. As discussed earlier, these authors considered this as a surprising result. We shall present a tentative interpretation of the same. How-

ever, the discussion presented here is more in the spirit of the mode-coupling theory which focuses on the calculations of the time correlation functions necessary to obtain the transport properties.

The organization of the rest of the paper is as follows. In the next section we present the main theoretical discussions. In Sec. III we present calculations of the activation energy of the cavity formation. Here we also present the calculations of the barrier frequency. In Sec. IV we present two different calculations of the frequency dependent friction. In Sec. V numerical results are presented. Section VI concludes with a discussion of the results.

II. THEORETICAL CONSIDERATIONS

The self-diffusion coefficient of a tagged particle is given by the following well known expression:

$$D = (1/6) \lim_{t \to \infty} \left[\frac{r^2(t) - r^2(0)}{t} \right], \tag{2}$$

where $r(t)$ is the position of the tagged particle at time t. The calculation of the displacement over a long time range is prohibitively difficult, especially in a complex supercooled liquid. However, due to extensive computer simulations[16–18] we know some aspects of the average properties of the trajectory of the particle. Initially, the tagged particle rattles around a cage made by its neighbors. A continuous slow diffusion of the particle occurs due to the relaxation of the cage. There are, however, occasional long jumps by the particle when the particle travels by about a molecular diameter. Such jumps are rare. The main contribution to the displacement function $[r^2(t) - r^2(0)]$ thus comes from these two kinds of motions in a dense liquid. The first is the collective structural relaxation of the neighbors which leads to a slow drift of the particle. This can be described as a continuous time random walk. The infrequent sojourns of the particle over relatively large distances appears to be activated in origin, as these long "jumps" are rare because they would certainly involve large activation energies. Recent computer simulations have made the presence of these jumps clear. It is important to realize that these jumps are present in dense, normal liquids much above the glass transition temperature where viscous mechanism dominates. In that range not only the hopping mechanism may be too slow to compete, but its rate itself may also show inverse viscosity dependence, as discussed below. Only when the viscosity of the liquid becomes so large that the viscous mechanism of transport becomes inefficient then does the hopping mechanism becomes relevant. The important question is why the hopping mechanism also does not become slow at large viscosities? This is particularly intriguing because the activation barrier for hopping should increase as the temperature is decreased.

From the general arguments presented here we assume that the time dependent probability distribution $P(\mathbf{r},t)$ obeys the following kinetic equation:

$$\frac{\partial P(\mathbf{r},t)}{\partial t} = D_{MC} \nabla^2 P(\mathbf{r},t) - P(\mathbf{r},t)$$
$$\times \int d\mathbf{r}' k_{hop}(\mathbf{r} \to \mathbf{r}') f(\mathbf{r} - \mathbf{r}') + \int d\mathbf{r}' k_{hop}$$
$$\times (\mathbf{r}' \to \mathbf{r}) f(\mathbf{r}' - \mathbf{r}) P(\mathbf{r}',t), \tag{3}$$

where D_{MC} is the diffusion coefficient given by the hydrodynamic mode-coupling calculations and k_{hop} is the hopping rate from one particle minimum to another. The function $f(\mathbf{r})$ is a function that is strongly localized around the distance that the particle hops which is typically the nearest neighbor distance. This is a difficult equation to analyze. We shall assume that there exists for each jump a specific direction dictated by the saddlepoint of the potential energy surface. This direction then serves as the reaction coordinate. If we further approximate $f(\mathbf{r})$ as a delta-function centered at the center of the distribution of the hopping distance, then further simplification of Eq. (3) is possible. It is illuminating to consider the one-dimensional picture where the equation of motion is given by

$$\frac{dP(X,t)}{dt} = D_{MC} \frac{\partial^2}{\partial X^2} P(X,t) - 2k_{hop} P(X,t)$$
$$+ k_{hop}[P(X-a,t) + P(X+a,t)], \tag{4}$$

where a is the nearest-neighbor distance. At low viscosities, the collective diffusion will dominate and $P(X,t)$ will spread according to the hydrodynamic diffusion. But as viscosity becomes very large, the diffusion coefficient D_{MC} becomes very small and the hopping mode begins to compete. In this regime, one may obtain a bimodal distribution of $P(X,t)$ at intermediate times.

If we are interested in the long time diffusion coefficient of a tagged molecule, then we can coarse-grain the hopping contribution. The two contributions to the diffusion coefficient are additive and we can write the self-diffusion coefficient as

$$D = D_{MC} + D_{hop}, \tag{5}$$

with

$$D_{hop} = (1/6) k_{hop} a^2, \tag{6}$$

where the D_{MC} denotes the normal contribution calculable from the hydrodynamics modes, after invoking the mode-coupling, if necessary, but without involving hopping. The second term is the contribution due to hopping. Note that because of the phenomenological nature of the above description, Eqs. (5) and (6) can be considered as approximations only; the previous discussions then provide the physical picture underlying this assumption. The important problems are the microscopic estimates of the two diffusion coefficients and their variation with temperature or density.

Next we proceed to make the estimates of the relative contributions. D_{MC} is inversely related to viscosity via the Stokes–Einstein relation. At temperatures away from the glass transition (still in the supercooled state), this term is expected to dominate, as the activation energy of the second process is very large (an estimate is provided later). How-

ever, when the viscosity rapidly becomes large as glass transition is approached, the situation may change.

What we really have to understand is the reason why the hopping mode of transport survives at large viscosities. Now, if the Smoluchowski rate expression is used in Eq. (6), we find that both the hydrodynamic and the hopping mechanism become equally inefficient as the viscosity rapidly increases near the glass transition. And, this is the dilemma that we next solve.

The main point is that the rate in an activated process is not given by the Smoluchowski limit expression, but by a generalization proposed sometime ago by Grote and Hynes.[8] In this generalization of the Kramers' theory, the non-Markovian or memory effects are taken into account. The resultant rate is given by the following expression:

$$k_{hop} = k_{GH} = (\lambda_r / \omega_b) k_{TST},$$ (7)

$$k_{TST} = (\omega_R / 2\pi) \exp(-E_{act}/k_B T),$$ (8)

and the reactive frequency λ_r is given by the following self-consistent relation:

$$\lambda_r = \frac{\omega_b^2}{\lambda_r + \zeta(\lambda_r)},$$ (9)

where $\zeta(\lambda)$ is the frequency dependent friction which describes the viscoelastic response of the dense liquid. The main idea behind the Grote–Hynes theory is that in an activated process the rate of barrier crossing is determined partly by the curvature of the barrier top. For a sharp barrier only the high frequency viscoelastic response, rather than the zero frequency viscous response, is probed. Thus, even if the macroscopic viscosity of the medium can become very large, an activated process can still proceed with a significant rate.

Therefore, if the Grote–Hynes expression is used in Eq. (5) for D_{hop}, it is clear than hopping process can be weakly dependent on macroscopic viscosity, in contrast to D_{MC} which will depend on structural relaxation. Thus, D_{hop} will become progressively more effective as viscosity becomes large near the glass transition. This explanation also offers the mechanism of decoupling of self-diffusion from viscosity. Note that we do not need to invoke a breakdown of ergodicity.

III. CALCULATION OF THE ACTIVATION BARRIER

We next find estimates of the average barrier height and the average barrier frequency in dense liquids. The model employed is shown pictorially in Fig. 1 where we have also shown the free energy diagram. The important thing to note is that the two minima for the particle configurations are separated by approximately a molecular diameter which is denoted by σ in all the subsequent discussions. Thus, the process of activation is the creation of a cavity next to the particle undergoing the hopping—the size of the cavity is only slightly bigger than the size of the particle itself. In the free energy diagram, the maximum (the barrier) corresponds to the transition state shown by the dashed circle in the figure above. This maximum is situated halfway between the two minima and more importantly, corresponds to the energy required to create the cavity of the minimum size.
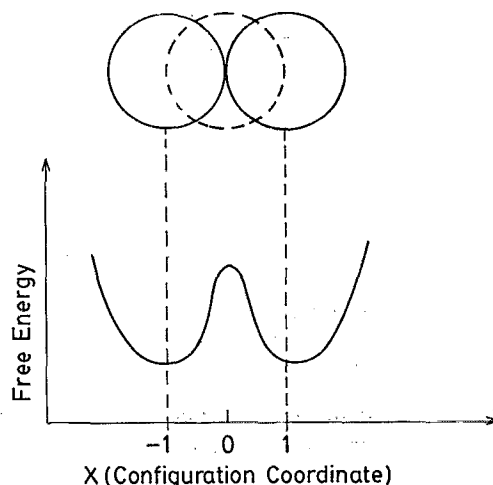

FIG. 1. A schematic representation of the free energy diagram as a function of the particle position (which is the reaction coordinate as discussed in the text) as it is moving towards the next minimum on the right. The height of the free energy is determined by the cavity size that is required. The dashed circle is the position on the top of the barrier.

The calculation of the activation energy for hopping is an old subject which has been dealt at length by Eyring and co-workers[19] in their theory of diffusion and has recently been revived in a more fundamental way by Zwanzig.[15] Eyring and co-workers estimate the free energy of hopping by relating it to the energy of vaporization of a molecule from the liquid to the vapor phase. This leads to an estimate of the hopping activation energy between 3–10 kcal/mol, the former for liquids consisting of nearly spherical molecules while the latter for polymeric liquids.[19] The method of Eyring may actually lead to an underestimation of the activation energy, as in a dense liquid the process of activation energy may be more involved. Therefore, the estimate of Eyring may give a lower bound of the activation energy.

Fortunately, there exists a more accurate way to calculate the free energy required to create a barrier within a dense liquid. This is the scaled particle theory (SPT) developed many years ago by Reiss et al.[9] We next describe the scaled particle theory (SPT) calculation. The SPT gives an analytic expression for the free energy to create a barrier if the system consists of hard sphere molecules only. Since in a dense liquid, molecules probe primarily the repulsive part of the intermolecular potential, we expect SPT to provide a fairly accurate estimate of the activation energy for nearly spherical molecules, except it may provide the upper bound. The free energy required to create a spherical cavity of radius r is given by

$$W(r,\rho) = -k_B T \ln(1 - 4\pi r^3 \rho/3) \quad \text{when } r < \sigma/2,$$ (10a)

and

$$W(r,\rho) = k_B T \rho \int_0^r d\lambda \, 4\pi \lambda^2 G(\lambda,\rho) \quad \text{when } r > \frac{\sigma}{2},$$ (10b)

where σ is the molecular diameter. The function $G(\lambda,\rho)$ is determined by the following equations:[9]

$$G(\xi,x)=\alpha_0(x)+\frac{\alpha_1(x)}{\xi}+\frac{\alpha_2(x)}{\xi^2},$$

with

$$\xi=r/2\sigma,$$

$$x=\rho\sigma^3,$$

$$\alpha_0(x)=p/(\rho k_B T),$$

$$\alpha_1(x)=2\sigma^2 S(x)/(x k_B T),$$

$$\alpha_2(x)=-4\sigma^2 S(x)\delta(x)/(x k_B T), \tag{11}$$

where ρ and p are the number density and the pressure, respectively. $S(x)$ and $\delta(x)$ are given by the following expressions:

$$S(x)=-\frac{k_B T\pi x^2(1+\frac{1}{6}\pi x)}{8a(1-\frac{1}{6}\pi x)}, \tag{12}$$

$$\delta(x)=\frac{1}{8}-\frac{1}{8}\left(\frac{1-\frac{1}{6}\pi x}{1+\frac{1}{6}\pi x}\right). \tag{13}$$

For the density dependence of pressure we may use the Carnahan–Starling equation of state[20] which provides an accurate description of the equation of state for hard spheres. For the Lennard-Jones system one may use computer simulations or the perturbation theory of liquids[21] to calculate the pressure. However, the SPT equations are strictly valid only for hard sphere systems only; for Lennard-Jones and other intermolecular potentials the free-energy values should be regarded as estimates only. In addition, the above description may have somewhat inaccurate temperature variation of free energy. However, for the general discussion it is alright to neglect the latter as a first approximation because the dynamic transition we are studying occurs over a small temperature interval when the static intermolecular correlations that determine the potential energy surface do not change significantly. As a result, the activation energy also changes insignificantly. Last, note that the scaled particle theory estimate of free energy of cavity formation depends significantly on the pressure term. For a hard spherelike system, pressure increases rapidly as the density is increased and this gives a large value of the cavity formation energy at high density. The situation can be different for complex molecular liquids which may have a weaker dependence of pressure on density. Thus, the cavity formation energy may be less for these liquids. This, of course, requires further quantification.

Next, we need to estimate the potential surface curvatures near the barrier and the well. This is, of course, prohibitively difficult and we need to make rather drastic approximations. Fortunately, the main conclusion of this work requires only correct estimates of the curvatures. First note that the curvature of the free energy near the minimum will be less than that near the barrier. However, an order of magnitude estimate of both can be obtained in the following way. We assume that the double-well can be approximated by the following simple form:

$$V(X)=E_{\text{act}}(X^2-a^2)^2. \tag{14}$$

Expression (10) gives the same value for the well (ω_R) and barrier (ω_b) frequencies, both given by (with $a=\sigma/2$),

$$\omega_R=\omega_b=4(E_{\text{act}}/M\sigma^2)^{0.5}. \tag{15}$$

For $\sigma=1$ Å and $E_{\text{act}}=5$ kcal/mol, the barrier (and the well) frequency is equal to 8×10^{13} s^{-1}. Furthermore, we expect ω_R to be less and ω_b to be more than this number. The hopping rate has rather complex dependence on these frequencies, as described by Eqs. (8)–(10). We shall approximate ω_R by Eq. (15), but shall set $\omega_b=2\omega_R$ in order to take into account the larger value of the former. This is certainly crude, but expected to be reliable.

IV. FREQUENCY DEPENDENT FRICTION

A crucial ingredient of the Grote–Hynes theory is the frequency dependent friction coefficient. An accurate calculation of this quantity is highly nontrivial not only because of the usual reason of obtaining the relevant time correlation function, but also because the contribution of the hopping mechanism to the friction coefficient still remains an intractable problem. For the present analysis, we shall perform two different model calculations. First, we use a mode-coupling calculation to obtain the friction kernel. An important aspect of this calculation is that it involves the dynamic structure factor of the liquid which shows anomalous behavior near the glass transition temperature. Second, we use the generalized hydrodynamic expression for frequency dependent friction. This function was provided originally by Zwanzig and Bixon[11] and has been used by many in the past.[22] The above implementation of Zwanzig–Bixon formulas ignores the hopping mechanism as Maxwell's viscoelastic model is assumed for the frequency dependent viscosity. This, however, expected to have a small effect, is discussed later.

A. Mode-coupling calculation

Here we shall use the time dependent density functional theory to obtain the expression for the friction—essentially the same expression can be obtained by more complicated methods. The rationale for using the density functional theory is that at the high density that we are interested in, the principal contribution to the friction comes from slow density relaxation.[1,6,10] The density functional expression for the free energy can be used to obtain the following expression for the effective potential acting on a tagged molecule at a given position[23]:

$$\beta V_{\text{eff}}(\mathbf{r},t)=-\int d\mathbf{r}'c(\mathbf{r}-\mathbf{r}')\delta\rho(\mathbf{r}',t), \tag{16}$$

where $c(\mathbf{r}-\mathbf{r}')$ is the two particle direct correlation function and $\delta\rho$ is the fluctuation in the number density of the liquid, defined by $\delta\rho(\mathbf{r},t)=\rho(\mathbf{r},t)-\rho$. The force acting on the molecule is obtained from $\mathbf{F}(\mathbf{r},t)=-\nabla V(\mathbf{r},t)$. The friction can be obtained from well-known Kirkwood's formula.[24] The final expression for the frequency (z) dependent friction is given by the following simple expression:

$$\zeta(z)=\zeta_b+\frac{k_B T}{6\pi^2\rho}\int_0^\infty dk\,k^4[\rho c(k)]^2 S(k,z), \tag{17}$$

where $S(k,z)$ is the dynamic structure factor, defined by

$$S(k,z) = \int_0^\infty dt F(k,t) \exp(-zt), \qquad (18)$$

and $F(k,t)$ is the intermediate scattering function

$$F(k,t) = \langle \rho_{-k} \rho_k(t) \rangle, \qquad (19)$$

where $\rho_k(t)$ is the Fourier transform of the density fluctuation. In Eq. (17) ζ_b is the bare friction, assumed to be given by the Enskog theory[24] and $c(k)$ is the Fourier transform of the direct correlation function. In deriving Eq. (17) we have neglected the self-motion of the tagged molecule. This can be easily included and the resultant expression is the same as given by Sjögren and Sjölander[10] in their seminal paper on mode coupling theory.

The important aspect of Eq. (17) is its dependence on dynamic structure factor. As the liquid is supercooled towards its glass transition temperature, the dynamic structure factor shows anomalous dynamics. Near the mode coupling "glass transition," $F(k,t)$ can be described by the following expression[11,24]:

$$F(k,t) = S(k) \exp\{-[t/\tau(k)]^\beta\}, \qquad (20)$$

where $S(k)$ is the static structure factor. The stretched exponential parameter β is typically between 0.5 and 1 and may be weakly k-dependent. We shall assume $\beta = 0.6$. The k-dependent relaxation time is not so easily expressible.[25] Fortunately, Eq. (17) explores dynamics primarily in the intermediate wave vector range where the following expression is approximately valid:

$$\tau(k) = [Dk^2/S(k)]^{-1}, \qquad (21)$$

where D is the diffusion coefficient of the liquid. Equations (17)–(21), if solved self-consistently, lead to a divergence of the zero frequency friction—a feature familiar in the mode-coupling theories of glass transition. For our purpose here, we shall merely assume that D is controlled by the mode coupling theories and that it goes to zero as

$$D = D_b(\rho_c - \rho)^\gamma, \qquad (22)$$

where the exponent γ is about 2 and ρ_c is the critical density and D_b is the bare diffusion coefficient which we take equal to $k_B T/\zeta_b$, where ζ_b is the bare friction, given by the Enskog theory.[24] In this work where we consider essentially hard spherelike systems, we assume $\rho_c \sigma^3 = 1.0$.

The above equations are expected to provide a reasonable description of the frequency dependent friction. The important point to note is that as the glass transition is approached, the diffusion coefficient becomes very small and the zero frequency (that is, macroscopic) friction becomes very small. However, the friction at large frequencies remains virtually unchanged.

B. Generalized hydrodynamic description

The generalized hydrodynamic expression for friction is rather complex. It is given by the following expression:[11,12]

$$\zeta(z) = \left(\frac{4\pi}{3}\right) \eta_s(z) R X^2 [2(X+1)P + (1+Y)Q], \qquad (23)$$
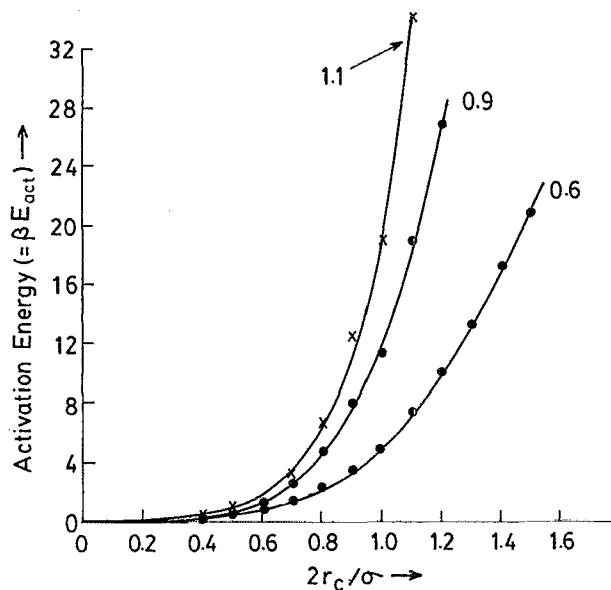

FIG. 2. The activation energy of cavity formation as a function of the cavity radius for a hard sphere fluid for three different values of the reduced density, $\rho^*(=\rho\sigma^3)$ which are shown in the figure. r_c denotes the cavity radius.

where R is the radius, $\eta_s(z)$ is the frequency dependent shear viscosity and P and Q are complex functions of many parameters. They include the shear and the bulk viscosities, the velocity of sound, the density of liquid, and the boundary condition (slip or stick). The quantities that deserve special attention are the frequency dependent shear and bulk viscosities, $\eta_s(z)$ and $\eta_v(z)$, respectively. These are assumed to be given by the following Maxwell relations:

$$\eta_{s,v}(z) = \frac{\eta_{s,v}(z=0)}{1+z\tau_{s,v}}. \qquad (24)$$

The dependence of the relaxation times on temperature and other parameters has been discussed in Ref. 26. As the viscosity of the medium increases, the viscoelastic relaxation times increases and the friction becomes large at small frequencies. It is interesting to note that this aspect is similar to the mode coupling calculation described above.

V. NUMERICAL RESULTS

Here we present numerical results using the correlation functions of the hard sphere system. These are not only analytically accessible but should also be applicable for small rigid molecules. As shown by the perturbation theories of liquids,[21] a soft-sphere or a Lennard-Jones system can be mapped into a hard sphere system by using a suitable temperature and density dependent hard sphere diameter.

In Fig. 2 we show the activation energy of cavity formation as a function of the cavity radius for three different values of the reduced density. As can be seen from the figure, the energy increases rapidly as the radius of the cavity becomes comparable to or larger than the radius of a liquid molecule. In addition, the activation energy of cavity formation increases rapidly with density. The latter plays an important role in the crossover mechanism addressed here, as we
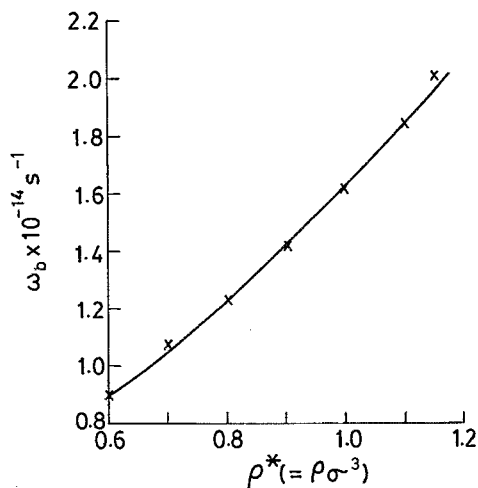
FIG. 3. The variation of the barrier frequency [as given by Eq. (15) of the text] with the reduced density of the liquid. Here the barrier is calculated for a cavity of size equal to the molecular diameter.
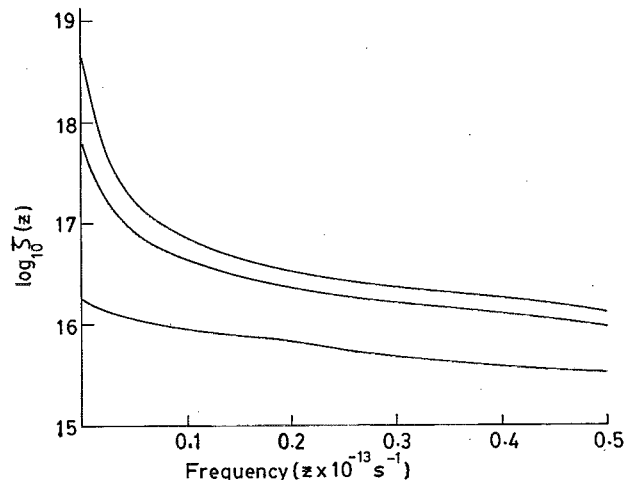

FIG. 4. The frequency dependence of the friction calculated by using the mode-coupling theory for three different densities. Here we have used Eqs. (17)–(21). The parameter values are given in the text. The structure factor has been assumed to be given by the Percus–Yevick equation (Ref. 21).

discuss later. Another point of interest is that the activation energy required to create a cavity of molecular size at density $\rho\sigma^3 = 1$ (near the glass transition density in the hard sphere liquid) is about $15\ k_B T$. This amounts to, at 200 K, an energy equal to 7.5 kcal/mol which is in fair agreement with the estimates made by Eyring many years ago. In Fig. 3, we show the variation of the calculated barrier frequency against the density of the liquid. The frequency increases steadily with density. Note that the barrier frequency is rather large even at the density $\rho\sigma^3 = 0.8$. Figures 2 and 3 represent two important results of this work. Note that the free volume theory also requires the activation energy for free volume formation which is similar to, if not identical with, the activation energy of cavity formation. However, the microscopic calculation of this energy by using the scaled particle theory helps in making the concepts quantitative.

In Fig. 4 we show the frequency dependence of the friction calculated by using the mode coupling theory [Eq. (17)] at three different densities, including one near the glass transition temperature, here assumed to occur at the reduced density 1.0. Note the sharp rise in the friction near the zero frequency for densities 0.95 and 0.98. Clearly, the macroscopic friction becomes very large near the glass transition temperature, which is expected. Another important feature is that the behavior at large frequencies are rather similar at the three densities. Thus, no signature of the impending viscosity (or frictional) catastrophy is present at the large frequencies. Note also that the friction shows a weak dependence on frequency at density 0.8 which is rather far from the glass transition temperature and has a rather small value of the zero frequency friction.

In Fig. 5 we show the frequency dependence of the hydrodynamic friction coefficient calculated by using the Zwanzig–Bixon expression, at three different values of the macroscopic viscosity. In this case we could calculate the behavior for a realistic liquid (in this figure we show the behavior of liquid octane) at somewhat smaller values of the

viscosity for which all the parameter values necessary to evaluate Zwanzig–Bixon friction are available directly from experiments.[26] This figure demonstrates the rapid variation of the friction as a function of frequency and that at the frequencies relevant here the friction is much smaller than the macroscopic friction. Note that both at large and small values of zero frequency friction, the frequency dependence is similar for mode-coupling and Zwanzig–Bixon friction.

We next use the above information to calculate the hopping rate and the diffusion constant. In order to carry out such a calculation we need the minimum size of the cavity that must be created for hopping to take place. The calculation of this size is a nontrivial problem. It can be easily
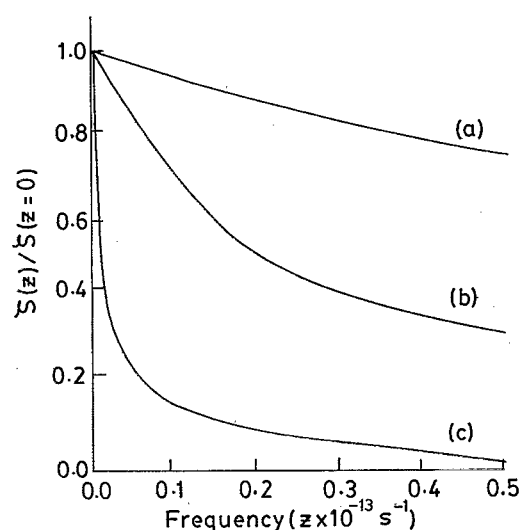

FIG. 5. The frequency dependence of the hydrodynamic friction calculated by using the Zwanzig–Bixon expressions, using the slip boundary condition. These results are for liquid octane using the values of shear and bulk viscosities and other ultrasonic parameters are taken from Ref. 26.
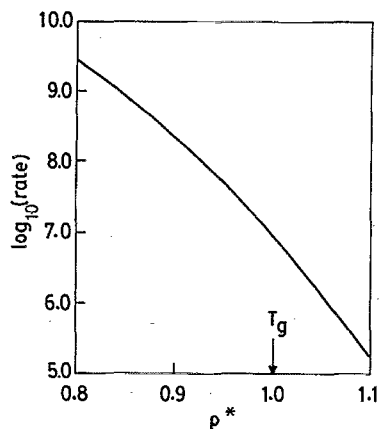
FIG. 6. The variation of the hopping rate with the reduced density (ρ^*) of a hard sphere liquid is shown in a log–log plot. The rate has been calculated by using the Grote–Hynes theory by assuming a cavity of radius equal to molecular radius. We have assumed that $\omega_b = 2\omega_R$. The glass transition has been assumed to be at $\rho^* = 1.0$. The rest has been discussed in the text.

FIG. 8. The variation of the total diffusion coefficient is plotted against the reduced density. The parameter values are the same as in Figs. 5 and 6.

understood from considering Fig. 1 that the size of the cavity should be slightly larger than the size of the molecule itself, in a one component system. An upper estimate can be obtained if we consider the required volume as that given by a cube of size σ (σ is the molecular diameter) and then equate the volume of the cube to that of a sphere. This gives the radius of the cavity equal to 0.62 σ. We, therefore, consider it reasonable and safe to assume that the radius of the minimum size cavity is between 0.5 σ and 0.6 σ. The details of the results discussed below depend on the choice of this size, although qualitative conclusions do not.

In Fig. 6 we show the variation of the hopping rate with the density of the hard sphere liquid. The rate has been calculated by using the Grote–Hynes theory with the calculated potential parameters and the mode-coupling theory result for frequency dependent friction. We have also used Eq. (6) for the diffusion coefficient. In Fig. 7 we plot the calculated hopping diffusivity against the calculated zero frequency

friction. There is a clear relation between them at lower densities, but the former becomes independent of the latter as the mode-coupling glass transition is approached.

We now use all these results to calculate the total diffusion coefficient, as given by Eq. (5). The results are shown in Fig. 8 where the total diffusion coefficient is plotted against the density. Beyond the mode-coupling glass transition (shown by an arrow in the figure), the hydrodynamic diffusion is zero, but still a small mass transport persists because of the hopping diffusion. This is quite similar to the result obtained in computer simulations by Madan, Keyes, and Seeley.[7,16] Figure 8 is an important result of this work and the nature of this graph is in qualitative agreement with the known facts. The small value of the diffusion coefficient in the "glassy state" is primarily due to the large activation barrier for cavity formation in a hard sphere system. We expect the value to be larger in a molecular liquid, like pentane.

We can now address the question of suddenness of the change of diffusive mechanism, as observed in experiments. Two factors combine to give this sudden crossover. First, the hopping mechanism itself decreases as the density is increased mainly due to the increase in the activation energy. So, the viscosity of the liquid must increase faster to make the hydrodynamic diffusion slower. This happens only when the viscosity increases rapidly near the mode-coupling transition.

Note that this hopping is a cooperative process even near the glass transition, as a hopping requires the creation of a favorable configuration which involves many molecules. While the static aspect of this configuration can be described in terms of the activation energy and barrier curvature, the dynamics of formation of this configuration is highly non-trivial. The description adopted here provides only a simplified description of this complicated process.

In the present discussion we have separated the diffusion into two parts. This separation is based primarily on a time scale argument. Note further than one can (and probably one
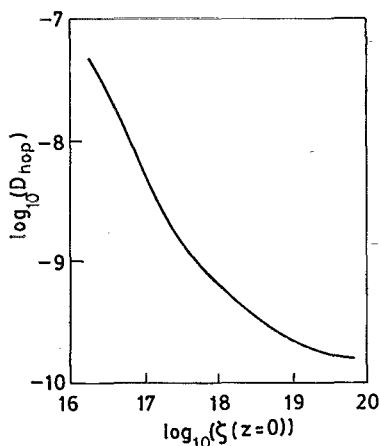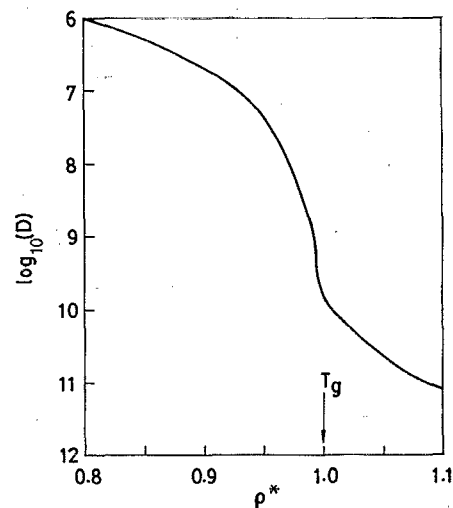

FIG. 7. The variation of hopping diffusivity is plotted against the zero frequency friction. The latter has been calculated by using Eqs. (17)–(21). The rest of the parameters are the same as in Fig. 6.

should) have a length scale argument too. Actually, in principle, one should have a viscosity (or friction) that depends on both length and time (via frequency and wave vector dependence). This is possible by adopting a more general mode coupling treatment. In the present mode coupling argument, we separate the liquid dynamics in two parts—the binary collision part which is short time and "local" and the collective part which contains the rest. It is the former that participates in the hopping mechanism because the barrier is sharp—the collective part is mostly a spectator in the hopping process. This, in essence a length scale argument does enter through the time scale argument.

We now turn to the important work of Keyes and co-workers,[7,16] especially to the surprising result that it is the low viscosity rather than the Smoluchoski-limit expression that provides a satisfactory description of the observed temperature dependence of the diffusion coefficient. The important point is that the imaginary frequencies (which are essentially the barrier frequencies) are also rather large in the simulations of Seeley et al.[7,16] Therefore, the logic outlined above for the decoupling of hopping from macroscopic viscosity also applies for the transitions over these barriers. There can, moreover, be a deeper connection between the approach of Stillinger–Zwanzig–Keyes and the approach adopted here. As the liquid becomes increasingly sluggish near the glass transition, the transitions across the barriers, especially the ones that will contribute to self-diffusion, will be dominated by the hopping of single particles over the potential barriers. Thus, the two approaches become similar near the glass transition temperature.

VI. CONCLUSION

Let me first summarize the main features of this work. We have addressed the reason for the crossover of the mechanism of mass transport from a hydrodynamic, viscosity dominated regime to an activated viscosity-independent hopping regime. Such a crossover has been observed both in experiments and in computer simulations. The present study provides a simple microscopic interpretation for this crossover. The interpretation is based on the observation that the activation energy barrier for hopping transport is rather large at high densities in a liquid. As the density of the liquid is increased (or the temperature is decreased) towards the glass transition region, this activation energy increases rapidly, as shown in Fig. 2. Since the distance of hopping remains virtually unchanged, this increase in barrier height implies an increase in the curvature of the potential surface (called the barrier frequency) at the maximum, that is, at the potential barrier. Now, this barrier frequency determines the "residence time" of the molecule near the activation barrier. As the barrier frequency becomes large, this "residence time" becomes short. Thus, the barrier crossing probes only the short time or the high frequency response of the liquid. This high frequency response, however, is not determined by the bulk or the macroscopic viscosity which is populated by the low frequency modes. As the glass transition is approached the viscosity becomes very large, but the high frequency motions are insignificantly affected. Thus, the hopping transport becomes decoupled from the bulk viscosity near the glass

transition. This is also the reason why hopping transport wins over the viscous mechanism in this regime. The important point we want to make about this crossover is that the hopping mechanism also becomes less and less efficient as the glass transition is approached. It is only because the viscosity rises in a divergencelike fashion that the crossover becomes noticeable.

In this article we presented detailed numerical calculations for the diffusion coefficient. Novel features of this calculation are the use of the scaled particle theory to obtain the activation energy of hopping and the non-Markovian rate theory to calculate the rate of hopping. The calculated diffusion coefficient shows the crossover only very close to the viscosity catastrophy that occurs near the glass transition temperature.

In order to establish a quantitative connection between the present work and that of Stillinger–Zwanzig–Keyes, we need to address some deep issues regarding the dynamics of a supercooled liquid. Let us start by quoting from Zwanzig's paper, "I present here a new and speculative derivation of a variant of the Stokes–Einstein formula, based on a particular view of cold dense liquids." It seems clear that Zwanzig's main hypothesis that "The liquid's configuration remains in one of the cells for a time, performing approximate harmonic oscillations about the liquid minimum, until it suddenly finds a saddlepoint or bottleneck on the potential energy surface and jumps to another cell" is valid at the low temperature, probably in the supercooled liquid. This is where the hopping mechanism may work. For the cell jumps to be identifiable as jumps, they must travel some distance in the configuration space. But the jumps considered in this paper and the ones in Stillinger–Zwanzig–Keyes formulation are different.

It is true that a variant of the Stokes–Einstein law relating diffusion and viscosity can be derived from hopping mechanism—it was actually done by Eyring and co-workers 50 years ago (Zwanzig himself made an interesting comment on this in the 1983 ACS Meeting). What I mean by "hydrodynamics" here is the gradual, infinitesimal displacements that is envisaged in the conventional hydrodynamics and also in the mode-coupling theory. This mode of mass transport is distinct from the hopping mechanism. Both may admit of a diffusion equation description in the long time and both can indeed be considered as hydrodynamic but the microscopic origin of them are different. A quantitative relationship between the calculations presented here and those based on Zwanzig's ideas is not available at present and will certainly be welcome.

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