PHYSICAL REVIEW E **68**, 051204 (2003)

Theory of the viscosity of supercooled liquids and the glass transition: Fragile liquids

Kyunil Rah and Byung Chan Eu
Department of Chemistry and Centre for the Study of Nonequilibrium and Nano Materials, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 2K6

(Received 23 June 2003; published 24 November 2003)

A statistical mechanical theory is presented for viscosity of relatively low molecular weight organic liquids which are supercooled down to the glass transition temperature. In this theory a relation resembling the Stokes-Einstein relation between the viscosity and self-diffusion coefficient of supercooled liquids and an expression for the self-diffusion coefficient are augmented by a suitably constructed semiempirical generic van der Waals equation of state that makes it possible to calculate the free volume. The theory accounts in excellent accuracy for viscosities and self-diffusion coefficients of fragile liquids over the entire range of temperature experimentally investigated. According to the theory, vitrification occurs when the free volume available for translational molecular motion falls below a critical value.

DOI: 10.1103/PhysRevE.68.051204 PACS number(s): 66.20.+d, 66.10.Cb, 61.43.Fs, 64.70.Pf

INTRODUCTION

Glassy substances have been known for four millennia. The modern scientific study [1] of glassy states traces back, at least, to several decades. Despite the long history of the subject matter and the importance of glasses in science and technology there are numerous aspects which have been defying a satisfactory understanding [2], especially from the viewpoint of statistical mechanics. Among them are the transport properties of supercooled liquids, such as the viscosity and diffusion coefficients, which characteristically change about 14 orders of magnitude as the system cools toward the glass transition temperature T_g without crystallization. Glass transition phenomena in general remain a major challenge in modern physical sciences [3].

The viscosity of supercooled liquids has been investigated with regard to the temperature dependence by employing the Stokes-Einstein relation. This relation was originally derived for a macroscopic spherical particle drifting in a viscous continuous medium by Stokes [4] and later by Einstein [5] who combined Stokes' hydrodynamic result with his Brownian motion theory result for diffusion to obtain the well-known relation between the viscosity η of the medium and the diffusion coefficient D of the particle,

$$\eta=\frac{k_BT}{3\pi\sigma_H D}. \tag{1}$$

Here k_B is the Boltzmann constant, T is the absolute temperature, and σ_H is the diameter of the particle. This relation, called the Stokes-Einstein (SE) relation and valid for a macroscopic size particle, says $\eta D/T$ is a constant independent of the density of the medium and temperature. It is found to be useful [6] even if the particle is comparable in size to the molecules of the medium for many molecular liquids, although there are also equally many exceptions [7] for which it does not work so well. Nevertheless, it has been applied to interpret the viscosity data of supercooled liquids and found to be useful if the temperature is well above the glass transition temperature. However, as the temperature is gradually lowered toward the glass transition temperature the SE relation is increasingly violated, and it becomes apparent that there should be an alternative to it to account for the experimental data on the temperature dependence of the viscosity of supercooled liquids.

A few years ago we have derived [8] by using a method of nonequilibrium statistical mechanics a relation between η and D, which resembles the SE relation but with the factor $\eta D/T$ depending on density and temperature in sharp contrast to the SE relation, which predicts it to be a constant. The relation derived does not require the diffusing particle to be of a size much larger than the molecules of the medium in contrast to the SE relation. The proportionality factor in question is given in terms of the intermolecular interaction force and the pair correlation function. Therefore it can be calculated by means of statistical mechanics as accurately as desired from the knowledge of intermolecular force and the pair distribution function. The SE-like relation mentioned was found to be excellent in accounting for the viscosity data of simple [9] as well as molecular [10] liquids with regards to their density and temperature dependence, provided that the self-diffusion coefficient is suitably supplied either empirically or through computer simulation methods.

In this paper we adopt the same method for supercooled liquids and develop a relation of viscosity and self-diffusion coefficient, which is calculated according to the modified free volume theory [11] of diffusion. In the modified free volume theory the self-diffusion coefficient is given in terms of the pair correlation function, which appears in the generic van der Waals (GvdW) equation of state [12] for pressure. Therefore, the viscosity and the self-diffusion coefficient of supercooled liquids can be calculated, either if the pair correlation function is available or if the GvdW equation of state is available by some means, for example, empirically.

Transport data of supercooled liquids are vexingly diverse and appear rather complex, displaying a varying temperature dependence from material to material. Angell [13] has introduced the notion of fragility of supercooled liquids and has thus brought a degree of order to the complex situation. The theory developed here will be shown to account for the experimental data, especially, for ''fragile'' glass forming liq-

1063-651X/2003/68(5)/051204(8)/$20.00

uids with a single set of expressions for the viscosity, self-diffusion coefficient, and GvdW equation of state.

This paper is organized as follows. In Sec. II the theory of viscosity will be developed for supercooled liquids on the basis of the theory previously developed for simple liquids in the normal states by employing a square well (SW) potential model. A square well potential is assumed for the sake of an analytic formula for the viscosity, which facilitates further development of the theory, which otherwise would not have been possible. Given the complex problem of supercooled liquids and vitrification, there is a great advantage to having analytic formulas for the transport coefficients, but once the things are better understood one may employ a continuous potential model, such as the Lennard-Jones potential, which can be implemented by a numerical method from the outset. In Sec. III the result for the self-diffusion coefficient in the modified free volume theory is presented. Since the modified free volume theory has been already reported in the literature this section is a brief review dedicated to the basic notion and the definitions of important quantities.

The self-diffusion coefficient in the modified free volume theory requires the GvdW parameters [12] and, especially, the one related to the excluded volume. This is the quantity necessary to calculate the transport coefficients, but, if the liquid is deeply supercooled, not readily calculable by means of computer simulation methods for the technical reason discussed later at the appropriate stage. Therefore a semiempirical model appears to be the only option for us to take. A construction of a semiempirical model for the GvdW parameter of fragile liquids will be discussed in detail in Sec. IV. Then equipped with all the mathematical tools necessary for the transport coefficients we calculate the viscosities and self-diffusion coefficients of typical fragile supercooled liquids and compare the results with experimental data available in the literature in Sec. V. Concluding remarks are given in Sec. VI.

RELATION OF VISCOSITY TO SELF-DIFFUSION COEFFICIENT

By employing a method of nonequilibrium statistical mechanics the viscosity of a spherical fluid can be shown [8] to be given by the expression

$$\eta = \eta_k(T) + \frac{\rho^2}{6D}\,\omega(\rho,T), \tag{2}$$

where η_k is the kinetic part, D is the self-diffusion coefficient, and

$$\omega(\rho,T) = \frac{2\pi}{15}\int_0^\infty dr\, r^5 u'(r) g(r)\,\theta(\xi - r). \tag{3}$$

Here r is the relative distance between two molecules, $u'(r) = du(r)/dr$ denotes the derivative of the intermolecular potential $u(r)$, $g(r;\rho,T)$ is the equilibrium pair correlation function, and $\theta(x)$ is the Heaviside step function defined by

$$\begin{aligned}\theta(x) &= 0 \quad \text{for} \quad x<0\\ &= 1 \quad \text{for} \quad x>0.\end{aligned}$$

The parameter ξ takes into account [8,9] the *finiteness* of the range of density fluctuations around the molecule of attention. The kinetic part η_k of viscosity is given by the Chapman-Enskog (CE) formula for the viscosity of a dilute gas and is independent of density. Since D also tends to the CE self-diffusion coefficient [14] as $\rho \to 0$ the viscosity formula in Eq. (2) tends to the CE viscosity for the dilute fluid in the limit of $\rho \to 0$. On the other hand, as ρ increases, the second term in Eq. (2), namely, the potential energy dependent term, becomes dominant in the liquid density regime. In fact, as the density increases η_k becomes so negligible compared to the second term that it is a very good approximation to simply drop η_k in the liquid density regime. Thus we have for the liquid viscosity the formula

$$\eta = \frac{\rho^2}{6D}\,\omega(\rho,T). \tag{4}$$

This will be the starting point for the derivation of the viscosity formula used for supercooled liquids in this work.

For the sake of deriving an analytic formula we assume an SW potential to represent the intermolecular interactions, namely,

$$u(r) = u_h(r) + u_a(r),$$

where

$$\begin{aligned}u_h(r) &= \infty \quad \text{for} \quad r<\sigma\\ &= 0 \quad \text{for} \quad r>\sigma,\end{aligned}$$

$$\begin{aligned}u_a(r) &= 0 \quad \text{for} \quad r<\sigma\\ &= -\varepsilon \quad \text{for} \quad \sigma<r<\lambda\sigma\\ &= 0 \quad \text{for} \quad r>\lambda\sigma,\end{aligned}$$

with σ denoting the size (molecular diameter) parameter, and ε and $\lambda\sigma$ the depth and width of the potential well, respectively.

By introducing the cavity function

$$y(r;\rho,T) = \exp[\beta u(r)]\, g(r;\rho,T), \tag{5}$$

where $\beta \equiv 1/k_B T$, and performing integration over r we obtain

$$\begin{aligned}\omega(\rho,T) = \frac{2\pi\sigma^5}{15\beta}\{&(e^{\beta\varepsilon}-1)[\lambda^5 y(\lambda\sigma)\,\theta(\xi-\lambda\sigma) - y(\sigma^+)]\\ &- y(\sigma^-)\}.\end{aligned} \tag{6}$$

Here the first term on the right is the contribution from the well of the potential, and the second term is the contribution from the hard core. We find that the cavity function $y(\sigma^+) = y(\sigma+0)$ in the first term should be distinguished from the cavity function $y(\sigma^-) = y(\sigma-0)$ in the second term with regard to their relation to the correlation function. We define the cavity function $y_h(r)$ by $y_h(r)=\exp[\beta u_h(r)]g(r)$. The cavity function $y(\sigma^+)$ is attributed mainly to $u_a(r)$, but it is approximated by $y(\sigma^+)\simeq\exp(-\beta\varepsilon)y_h(\sigma)$, whereas we approximate $y(\sigma^-)$ by $y(\sigma^-)\simeq y_h(\sigma)$. The cavity function $y_h(\sigma)$ is then related to the GvdW parameter associated with the excluded volume and will be calculated by means of Eq. (20) below; see Eqs. (19) and (20) below for the role of the cavity functions in the present theory.

Since the density fluctuation range ξ is not well defined and has a distribution, it is appropriate to introduce the distribution function $P(\xi)$ for ξ. Since the range of ξ must be from 0 to ∞ the distribution function $P(\xi)$ is normalized as follows:

$$\int_0^\infty d\xi P(\xi)=1. \tag{7}$$

Then averaging the expression for $\omega(\rho,T)$ in Eq. (6) of the distribution of ξ we obtain

$$\omega(\rho,T)=\frac{2\pi\sigma^5 y_h(\sigma)}{15\beta}S(\rho,T), \tag{8}$$

where

$$S(\rho,T)=\lambda^5\Theta(\rho,T)(e^{\beta\varepsilon}-1)\frac{y(\lambda\sigma)}{y_h(\sigma)}-(2-e^{-\beta\varepsilon}), \tag{9}$$

with $\Theta(\rho,T)$ defined by

$$\Theta(\rho,T)=\int_0^\infty P(\xi)\theta(\xi-\lambda\sigma)d\xi=\int_{\lambda\sigma}^\infty P(\xi)d\xi. \tag{10}$$

The quantity $\Theta(\rho,T)$, which is the mean value of $\theta(\xi-\lambda\sigma)$, is clearly $0\leqslant\Theta\leqslant1$. It is a factor contributing to $\omega(\rho,T)$, which is essentially related to the force per unit area exerted by the molecules beyond the distance $\lambda\sigma$ to the molecule of attention. It is simply the probability of ξ being larger than $\lambda\sigma$. The larger the Θ, the larger and more spread out the effective range of density fluctuations. In particular, $\Theta=0$ means that the density fluctuations around the molecule of attention are completely confined within the range of radius $\xi\simeq\lambda\sigma$. For the distribution function $P(\xi)$ the following stretched exponential form is postulated to hold:

$$P(\xi)=\frac{\theta(\xi-\sigma)}{\gamma\zeta(\rho,T)}\left(\frac{\xi}{\sigma}\right)^{\gamma-1}\exp\left\{-\zeta(\rho,T)\left[\left(\frac{\xi}{\sigma}\right)^{\gamma}-1\right]\right\}, \tag{11}$$

where $\zeta(\rho,T)$ generally depends on both T and ρ, and γ is an exponent. The step function $\theta(\xi-\sigma)$ is inserted because there is no density fluctuation possible if $\xi<\sigma$. It then follows from Eq. (10),

$$\Theta(\rho,T)=\exp[-\zeta(\rho,T)(\lambda^\gamma-1)]. \tag{12}$$

Because there is as yet no statistical mechanical theory for $P(\xi)$, the associated parameters are treated empirically in the present work. However, it turns out that, as will be shown, $S\simeq0.7$ almost invariably for many liquids, and this almost universal constancy of S removes the necessity of an explicit empirical treatment of Θ. This constancy of S, in fact, provides a way to estimate $\Theta(\rho,T)$ backward and $P(\xi)$ by using Eq. (9), and from the information it is possible to extract the average size of "clusters" formed, if any, around the molecule of attention, as the system supercools towards the glass transition temperature. This aspect of $\Theta(\rho,T)$ in relation with η seems potentially useful for learning about the structure of supercooled liquids near the glass transition temperature by examining their transport data. We defer its study to the future.

Collecting the results regarding the viscosity–self-diffusion coefficient relation we have the expression

$$\eta=\frac{\pi\sigma^5 k_BT}{45D}\rho^2 y_h(\sigma)S(\rho,T)\simeq\frac{0.7\pi\sigma^5 k_BT}{45D}\rho^2 y_h(\sigma). \tag{13}$$

This relation resembles the SE relation, but significantly differs from it because of the density and temperature dependent coefficient, which makes a crucial difference in accounting for the temperature and density dependence of the viscosity of supercooled liquids, as will be shown.

SELF-DIFFUSION COEFFICIENT

The viscosity formula (13) suggests that, apart from the factors related to Θ, the viscosity of supercooled liquids can be calculated if the self-diffusion coefficient is known. One way of calculating the self-diffusion coefficient is to use the free volume theory of Cohen and Turnbull [15], which yields D in the form

$$D=g\bar{u}a(\rho)\exp\left(-\alpha\frac{v^*}{v_f}\right), \tag{14}$$

where g is a geometric factor, $a(\rho)$ is roughly the diameter of the cage created in the liquid, $\bar{u}$ is the gas kinetic speed, v^* is a critical volume just large enough to allow another molecule to move in as a void is created by a molecule on leaving its position, v_f is the free volume, and α is a parameter of $O(1)$. The self-diffusion coefficient in the Cohen-Turnbull free volume theory is physically transparent and reasonable except for poorly determined parameters and the free volume that is difficult to calculate by means of statistical mechanics. Close examination of the formula in Eq. (14) suggests that v^* may be taken as the molecular volume $v_0=\pi\sigma^3/6$ and the factor $g\bar{u}a(\rho)$ in essence may be interpreted as the mean free path theory expression for diffusion. This interpretation immediately suggests that the factor may be expressed as the CE self-diffusion coefficient [14] of hard spheres of diameter σ,

$$g\bar{u}a(\rho)\equiv D_0=\frac{3}{8\rho\sigma^2}\sqrt{\frac{k_BT}{\pi m}}, \tag{15}$$

where m is the molecular mass. It is reasonable to assume a hard sphere model because hard repulsive interactions are in operation for the particles packed in close proximity to each other in liquids. This leaves only one adjustable parameter α, which is in practice found to be about unity. We will therefore take $\alpha = 1$ in this work. There now remains the question of free volume. The success of the free volume theory of diffusion hinges upon how free volume is calculated. Unfortunately, free volume is a delusive quantity, which has defied a definitive statistical mechanical representation and is consequently difficult to calculate accurately in a definite form in the statistical mechanics of liquids since it was originally introduced by van der Waals.

We have shown [12] that if there exist attractive and repulsive parts in the intermolecular potential energy or force the virial form of the equation of state can be rearranged to a form resembling the van der Waals equation of state,

$$(p + A\rho^2)(1 - B\rho) = \rho k_B T, \tag{16}$$

where A and B are density and temperature dependent parameters which have rigorous statistical mechanical representations, as will be shown shortly for the particular case of the SW potential. This form of equation of state is called the GvdW equation of state. The parameters A and B are called the GvdW parameters. The parameter A is related to the attractive potential energy, and B to the repulsive potential energy. Therefore B is a measure of excluded volume of the fluid. This GvdW equation of state therefore allows the natural definition of free volume [12],

$$v_f = v[1 - B(\rho,T)\rho], \tag{17}$$

where $v = 1/\rho$. In this manner, in our previous papers [16–18] on diffusion we have been able to modify the free volume theory formula of the Cohen-Turnbull theory for the self-diffusion coefficient D of liquids into the form

$$D = \frac{3}{8\rho\sigma^2}\sqrt{\frac{k_B T}{\pi m}}\exp\left(-\frac{v_0\rho}{1 - B\rho}\right), \tag{18}$$

which is now made completely statistical mechanical because B can be calculated rigorously by means of statistical mechanics. In the SW potential model introduced earlier, the GvdW parameters $A(\rho,T)$ and $B(\rho,T)$ are given by the statistical mechanical expressions [12]

$$A^* = \frac{A}{\varepsilon v_0} = \frac{4}{\varepsilon\beta}(e^{\beta\varepsilon} - 1)[\lambda^3 y(\lambda\sigma) - y(\sigma^+)], \tag{19}$$

$$B^* = \frac{B}{v_0} = \frac{4y_h(\sigma)}{1 + 4\phi y_h(\sigma)}, \tag{20}$$

where $\phi = v_0\rho$ is the packing fraction. These are rigorous statistical mechanical representations of A and B, although for an SW potential. Therefore by Eq. (20) we now have a rigorous statistical mechanical representation of free volume, which can be calculated as precisely as the cavity function.

Thus the transport coefficients D and η can be calculated by means of statistical mechanics if formulas (18) and (13) are employed together with the information either on $y_h(\sigma)$ or on B. Unfortunately, there is no analytical theory available for the cavity function $y_h(\sigma)$ or B for liquids. Although they can be calculated accurately for ordinary liquids by computer simulation methods, for deeply supercooled liquids even the computer simulation methods are difficult to implement to a desirable accuracy because of technical limitations involved, such as the limited simulation time ($\sim 10^{-7}$ s) and the lower bound of the detectable self-diffusion coefficient being too large compared with the experimental value, which is $\sim 10^{-18}$ cm^2 s^{-1} at the glass transition temperature. These limitations conspire to yield rather inaccurate simulation results for transport coefficients. For this reason it is necessary to devise an alternative. We take a semiempirical approach and construct a model for B, which will then be validated in comparison with experiment.

It is also intriguing to note that, if Eq. (20) is made use of, the viscosity given by the second line of Eq. (13) can be expressed in the form

$$\eta = \frac{0.7 k_B T B^* \phi^2}{5\pi\sigma D(1 - B^*\phi)}, \tag{21}$$

which allows us to compute the viscosity from the information on D, T, ϕ, and the empirical density and temperature dependence of B, if the GvdW equation of state is empirically known for the supercooled liquids. In any case, the viscosity is computed by using the model for $B^*(\phi,T)$ developed below.

A MODEL FOR THE GvdW PARAMETER *B*

Because $y_h(\sigma)$ cannot be efficiently simulated for a deeply supercooled system, we look for a semiempirical way of calculating it. For the SW potential model adopted for this work the cavity function $y_h(\sigma)$ gets contributions from both the hard core and the attractive well part of the potential, and the hard core part is the major contribution when particles are closely packed. Therefore $y_h(\sigma)$ may be written as follows:

$$y_h(\sigma) = y_{hs}(\sigma) + \delta y_h, \tag{22}$$

where $y_{hs}(\sigma)$ is the cavity function of the hard sphere fluid of diameter σ and δy_h is the correction to $y_{hs}(\sigma)$ that arises from the attractive part of the potential. Whereas $y_{hs}(\sigma)$ is temperature independent, the correction term δy_h is temperature and density dependent. For this reason, although δy_h is generally small in magnitude at high temperatures, it is indispensable, and plays a crucial role, in accounting for the behavior of glass forming liquids near the glass transition temperature. On inserting Eq. (22) into the expression for B^* in Eq. (20) and expanding in δy_h we obtain

$$B^*(\phi,T) = B^*_{hs}(\phi)\left[1 + \frac{\delta y_h(\phi,T)}{y_{hs}(1 + 4\phi y_{hs})} + O(\delta y_h^2)\right], \tag{23}$$

where $B^*_{hs}(\phi)$ is the generic van der Waals parameter B^* for the hard sphere fluid,

$$B_{hs}^{*}(\phi)=\frac{4y_{hs}(\sigma)}{1+4\phi y_{hs}(\sigma)}.$$

If the Carnahan-Starling equation of state is used for B_{hs}^{*} we find the density dependence of B_{hs}^{*}:

$$B_{hs}^{*}(\phi)=\frac{2(2-\phi)}{1+\phi+\phi^{2}-\phi^{3}}. \tag{24}$$

In a previous work [19] on the generic van der Waals equation of state we have found that on the critical isotherm the quadratic model for $B^{*}(\phi,T)$,

$$B^{*}=B_{c}^{*}(1+b_{1}x+b_{2}x^{2}+b_{na}x^{\delta})\quad(x=\rho/\rho_{c}-1), \tag{25}$$

is excellent in accounting for the experimental data of the critical isotherms of argon and methane. In this expression for the quadratic model, b_1 and b_2 are parameters that can be uniquely determined in terms of critical parameters (ϕ_c,T_c,p_c) [20] and B_c^{*}, where B_c^{*} is the value of B^{*} at the critical point which is determined from the critical parameters or by simulations for $g(r)$ at $T=T_c$ and $\phi=\phi_c$; b_{na} is an adjustable parameter; and δ is one of the critical exponents, namely, $\delta\simeq 4.30$. Therefore by fitting the form for $B^{*}(\phi,T_c)$,

$$B^{*}(\phi,T_{c})=B_{hs}^{*}(\phi)\left(1+\frac{c_{0}}{1+c_{1}\phi^{6}}\right), \tag{26}$$

to the quadratic model in Eq. (25) we find the coefficients c_0 and c_1:

$$c_{0}=-\phi_{c}^{6}\left(1+\frac{6}{d_{1}}\right),\quad c_{1}=d_{0}(1+c_{0}\phi_{c}^{6}),$$

$$d_{0}=\frac{B_{c}^{*}}{B_{c}^{hs}}-1,\quad d_{1}=-\frac{1+d_{0}}{d_{0}}\left(\frac{B_{1}^{hs}}{B_{c}^{hs}}-b_{1}\right), \tag{27}$$

where

$$B_{c}^{hs}=\frac{2(2-\phi_{c})}{1+\phi_{c}+\phi_{c}^{2}-\phi_{c}^{3}},$$

$$B_{1}^{hs}=-\frac{2\phi_{c}(3+4\phi_{c}-7\phi_{c}^{2}+2\phi_{c}^{3})}{(1+\phi_{c}+\phi_{c}^{2}-\phi_{c}^{3})^{2}}. \tag{28}$$

For the temperature dependence of $B^{*}(\phi,T)$ away from the critical isotherm we look for B^{*} in the form

$$B^{*}(\phi,T)=B_{hs}^{*}(\phi)\left[1+\frac{c_{0}}{1+c_{1}\phi^{6}}f(T)\right]. \tag{29}$$

Here the function $f(T)$, describing the T dependence of B^{*}, is expressed by a function of scaled temperature T_g/T in the form

$$f(T)=f_{0}(T)\,\frac{\exp\left(\frac{\hat{\Theta}}{T_{g}}\sqrt{\frac{T_{g}}{T}}\right)-1}{\exp\left(\frac{\hat{\Theta}}{T_{c}}\sqrt{\frac{T}{T_{g}}}\right)-1}\quad\text{with}\quad\hat{\Theta}\simeq 430\,\text{K}, \tag{30}$$

with $f_0(T)$,

$$f_{0}(T)=\theta(T-T_{c})+\tanh[\mu(T_{g}/T)^{\vartheta}], \tag{31}$$

where μ and ϑ denote material dependent parameters. The parameter value for $\hat{\Theta}$ in Eq. (30) is determined by fitting Eq. (29) to B^{*} calculated by means of Monte Carlo (MC) simulations in the supercritical regime. The value for $\hat{\Theta}$ is found almost independent of the species considered and is thus almost universal. The fidelity of the temperature dependence of $f(T)$ has been successfully checked against the MC simulation results in the supercritical regime, as shown in a previous paper [18]. In the present work on supercooled liquids we assume that the mathematical form taken for $f(T)$ in Eq. (30) remains valid in the temperature range of supercooled liquids. We verify this assumption with comparison with experimental data on the viscosity and self-diffusion coefficient of fragile supercooled liquids in the following.

The potential parameters are required, in particular, to compute B_c^{*}, for example, by means of MC simulations. They are determined within the accuracy of the potential model employed, from the experimental second virial coefficient data. Experimental data [21] for the second virial coefficient $B_2(T)$ were fitted to the expression for the SW potential,

$$B_{2}(T)=(2\pi\sigma^{3}/3)\{1-(\lambda^{3}-1)[\exp(\beta\varepsilon)-1]\}, \tag{32}$$

in order to determine the SW potential parameters $[\sigma\ (\text{nm}),\varepsilon k_B^{-1}\ (\text{K}),\lambda]$ as follows: for toluene these are $(0.516,888,1.24)$. For lack of the second virial coefficient data on *O*-terphenyl (OTP) and salol their size parameters are determined by using $\phi_g=0.48$, where ϕ_g is the packing fraction of the supercooled liquid at T_g. The B_c^{*} computed from MC simulations performed with the aforementioned potential parameter sets is found to be 5.46.

Once c_0 and c_1 are known, the glass transition temperature T_g can be consistently determined within the framework of the present theory by solving Eq. (13) iteratively for the temperature at which the viscosity becomes 10^{12} Pa s, as is conventionally defined as the kinetic glass transition temperature. In this way, we have predicted T_g, as indicated in the figure for toluene with c_0 and c_1 determined from the quadratic model [18,19]; the predictions agree well with the experiment [22]. Note that $f_0\rightarrow 1$ as T tends to T_g. It is also noteworthy that T_g depends, although weakly, on the glass transition density ρ_g. For instance, an increase of density by 1% at T_g brings about a decrease of T_g by about 0.5 K owing to the corresponding decrease in viscosity, and this can be inferred from Eq. (29). This tendency is consistent with the phenomenon that a faster cooling leads to glass transition at

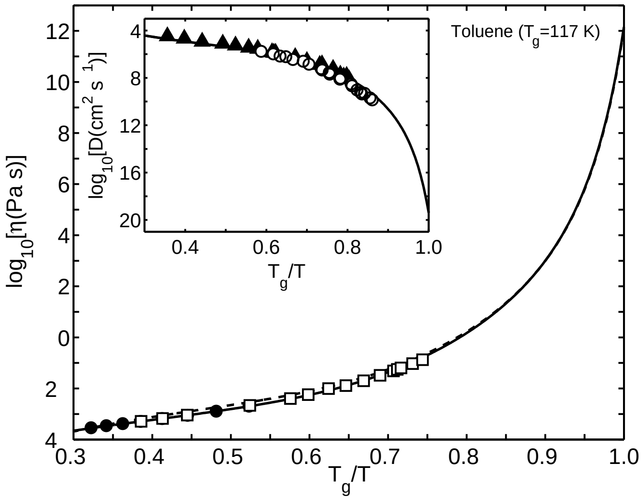

FIG. 1. Viscosity of toluene at 1 atm. The curves are calculated from the present theory, namely, Eqs. (13) and (18), where the solid curve is computed with Eq. (33), whereas the broken curve is with $S=0.70$. The symbols (□ [23] and ● [24]) are for the experimental data. As to $\rho(T)$ at 1 atm, an empirical formula [23] is used. The inset is for the self-diffusion coefficient of toluene, where the curve is calculated in Ref. [18] from Eqs. (18), (29), and (30) with $c_0=0.791$, $c_1(\phi_c)^6=0.185$, $T_g=117$ K, and $f_0(T)=\tanh[4.5(T_g/T)^4]$, whereas the symbols are the data [25,26] for D measured by a nuclear magnetic resonance technique.

a higher T_g but at a lower ρ_g. In the higher T regime, however, the viscosity increases with increasing ρ.

COMPARISON WITH EXPERIMENT

We can now calculate the viscosity of supercooled liquids from Eqs. (13) and (18) by assuming that the formula for B^* still holds in the low T regime down to T_g. In Fig. 1, we thus have calculated the viscosity profile for toluene in the temperature range from $T=3T_g$ down to T_g and have compared it with the available experimental data [23,24]. The associated $y_h(\sigma)$ is computed by equating Eq. (20) to Eq. (29), whereas $y(\lambda\sigma)$ involved in Eq. (9) is evaluated from Eqs. (16) and (19) by setting $p=1$ atm. As to the parameter $\zeta(\rho,T)$ appearing in the expression for $\Theta(\rho,T)$ in Eq. (12) we express it in the form

$$\zeta(\rho,T)=(\lambda^{\gamma}-1)^{-1}\zeta_0\left(\frac{T_g}{T}\right)\left[1-\zeta_1\left(\frac{T}{T_g}\right)^2\right],$$

where ζ_1 and ζ_0 are adjustable parameters determined empirically. With this form we have

$$\Theta(\rho,T)=\exp\left\{-\zeta_0\left(\frac{T_g}{T}\right)\left[1-\zeta_1\left(\frac{T}{T_g}\right)^2\right]\right\}. \tag{33}$$

By choosing $\zeta_0=7.1$ and $\zeta_1=0.016$ we have computed the solid curve for the viscosity in Fig. 1 with Eq. (33).

We have noticed that the resultant $S(\rho,T)$ in Eq. (9) remains virtually constant in the temperature and density range investigated. This has prompted us to replace S with a constant, namely, $S=0.70$, which turns out to perform well for all the liquids examined. The result so calculated is denoted by the broken curve in Fig. 1. Moreover, use of $S=0.70$ for other glass forming substances is tested to be sufficiently satisfactory, as shown in Figs. 2 and 3. We note that $\Theta(\rho,T)$ for toluene tends to $\sim 10^{-3}$ as T_g is approached, and it implies that an average cluster size near T_g, namely, $2\xi \simeq 2\lambda\sigma$ is estimated to be about 1.6 nm.

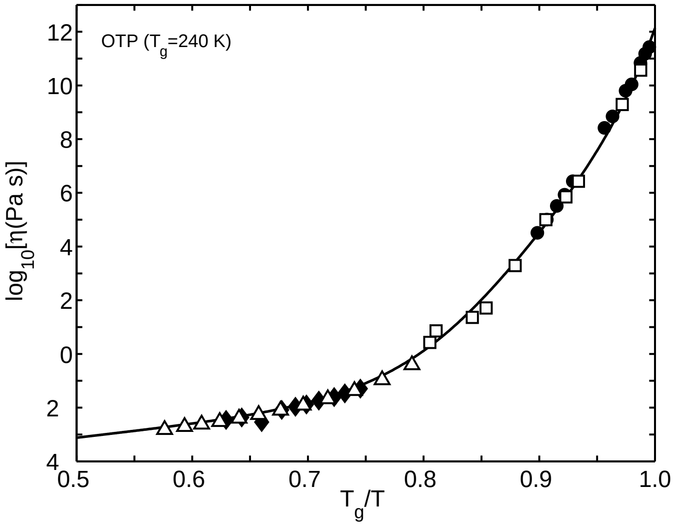

FIG. 2. Viscosity of OTP at 1 atm. The solid curve is computed from Eq. (13) with $S=0.70$, whereas the symbols are for the experimental data (□ [27], ♦ [28], △ [29], and ● [30]). An empirical equation [27] is used for $\rho(T)$ at 1 atm. The parameters used are $\sigma=0.680$ nm, $c_0=1$, $c_1(\phi_c)^6=0.0473$, $T_g=240$ K, and $f_0(T)=\tanh[4.6(T_g/T)^7]$.

Figure 2 shows the viscosity profile for OTP as a canonical fragile glass former. The viscosity profile calculated from Eq. (13) with $S=0.70$ compares excellently with the experi-

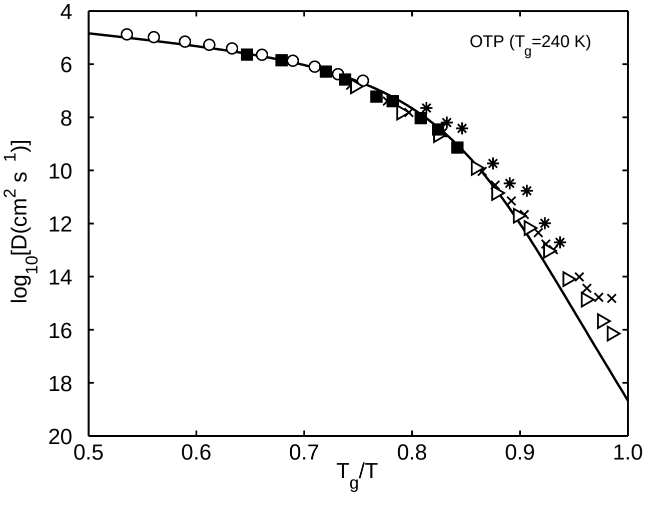

FIG. 3. Self-diffusion coefficients of *o*-terphenyl at 1 atm. The solid curve is predicted by using Eqs. (18) and (29) with $\mu=4.6$ and $\vartheta=7$. The symbols are for the experimental data for D of OTP: ○ from Ref. [31] and ■ from Ref. [32]. Various tracer diffusion coefficients in OTP are also shown, where ▷ are for the experimental data for D_t of TTI [32], × for ACR [32], and * for anthracene [33], respectively. See the text for the abbreviations.

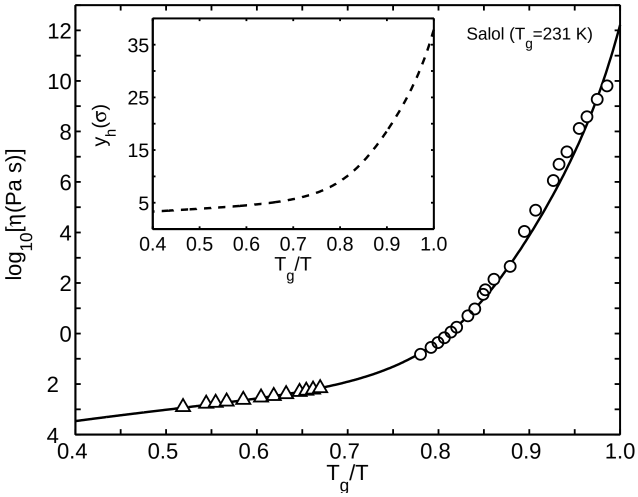

FIG. 4. Viscosity of salol at 1 atm. The solid curve is computed from Eq. (13) with $S=0.70$, whereas the symbols are for the experimental data (△ [29] and ○ [30]). The thermal expansion coefficient [29] for salol, $\alpha_p=7.95\times10^{-4}$, is used for $\rho(T)=\rho_m\exp[\alpha_p(T_m-T)]$, where $\rho_m=1.26$ g/cm^3 at $T_m=315$ K. In the inset the dashed curve is for $y_h(\sigma)$ computed from Eqs. (20) and (29) with $\sigma=0.621$ nm, $c_0=1$, $c_1(\phi_g)^6=0.133$, $T_g=231$ K, and $f_0(T)=\tanh[4.0(T_g/T)^7]$, where $\phi_g\doteqdot0.482$ is the packing fraction at T_g. The liquid-vapor critical temperature $T_c=714$ K is assumed in the absence of the information.

mental data [27–30], supporting the reliability of the present theory. The self-diffusion coefficient D predicted [18] from Eq. (18) and shown in Fig. 3 is also in good agreement with the experimental data down to the lower limit at $T\simeq1.2T_g$ of the measurements for D. It is noteworthy that as T is lowered to below $T\simeq1.15T_g$, the self-diffusion coefficient (solid curve) "decouples" from the tracer diffusion coefficients D_t in OTP of TTI [2,2′-bis(4,4-dimethylthiolan-3-one)] (△), ACR (7,7a-dihydro-2,4,7,7,7a-penta-methylbenzo-[*b*]-furan-5,6-dicarboxylic anhydride) (*), and anthracene (×). The deviation of D_t from D shown in the figure is beyond the experimental error bounds. The possible origin of such discrepancy, which reaches a factor of $\sim10^2$, especially, near T_g, was discussed in Ref. [18] based on the explicit relation [17,35] derived for D and D_t, where the average cluster size was estimated to be about 2 nm.

Figure 4 shows the viscosity of salol calculated from Eq. (13) with $S=0.70$ in comparison with the experiment [29,30]. The $y_h(\sigma)$ computed from Eq. (29) is shown (inset) to give an idea of how $y_h(\sigma)$ behaves as the system supercools towards the glass transition temperature, and it implies that molecules tend to get more closely packed as T_g is approached. Such a phenomenon is not observed at high temperatures even if the density is the same as ρ_g. Clustering tendency estimated in terms of $y_h(\sigma)$ appears to be larger, especially, near T_g, roughly by 2–3 times, than the case for hard sphere fluids [34]. This feature is attributed to the presence of attractive forces that are absent in hard spheres. A similar trend of $y_h(\sigma)$ is observed also for the cases of toluene and OTP.

By using the SE relation for a diffusing particle with hydrodynamic radius $r_H=\sigma_H/2$ and Eq. (13) we find the ratio of the diameters $R\equiv\sigma/\sigma_H=(42/25)\phi^2y_h(\sigma)$ for which $S=0.7$ is used. It is noticeable that, depending on T and ρ, the ratio R varies, for example, by about 25 times as fragile liquids (such as those considered in this work) supercool from $3T_g$ to T_g. Therefore this ratio is indicative of the defect of the SE relation in the sense that the $\eta D/T$ of the SE relation is independent of T and ρ, and we see the source of the so called decoupling of diffusion from viscosity observed and discussed in the literature. In contrast, Eq. (13) does not have such a deficiency because R depends on T and ρ.

CONCLUDING REMARKS

In this paper we have derived a statistical mechanical expression for the viscosity of supercooled liquids and have successfully tested its reliability against the experimental data for toluene, OTP, and salol. With a pair of statistical mechanical formulas for η and D and the semiempirical formula for B^* we are able to represent the temperature and density dependence of glass formers considered. Since they are only the glass formers classified as fragile liquids the model constructed for B is not as yet sufficiently comprehensive as to cover the whole range of fragility spectrum. Nevertheless, it can be inferred from the present theory that, as the glassy state is approached, free volume varies with density and temperature and vitrification occurs as the free volume available for diffusive motion of molecules falls below a critical value. The present model raises the hope that a more comprehensive model is possible to construct by gleaning the considerable insights into the complex problem of vitrification provided by the present model. When we are in possession of a computer simulation method that is capable of accurately handling deeply supercooled liquids the model may be disposed of. In the meantime, we believe, it can be of service to us in organizing experimental data on transport coefficients of fragile supercooled liquids.

ACKNOWLEDGMENTS

This work was supported in part by the Natural Sciences and Engineering Research Council of Canada and the FCAR of Quebec through the Center for the Study of Nonequilibrium and Nano Materials, McGill University.

---

[1] W. Kauzmann, Chem. Rev. (Washington, D.C.) **43**, 219 (1948).

[2] P.G. Debenedetti and F.H. Stillinger, Nature (London) **410**, 259 (2001).

[3] P.W. Anderson, Science **267**, 1615 (1995).

[4] G.G. Stokes, *Mathematical and Physical Papers* (Cambridge University Press, London, 1880), Vol. 1, pp. 38–43.

[5] A. Einstein, *Brownian Movement* (Dover, New York, 1956).

[6] H.J. Parkhurst, Jr. and J. Jonas, J. Chem. Phys. **63**, 2705 (1975); M. Fury, G. Munie, and J. Jonas, *ibid.* **70**, 1260 (1979).
[7] G. Pollack, Phys. Rev. A **23**, 2660 (1981); G.L. Pollack and J. Enyeart, *ibid.* **83**, 5861 (1985).
[8] K. Rah and B.C. Eu, Phys. Rev. E **60**, 4105 (1999); J. Chem. Phys. **112**, 7118 (2000).
[9] K. Rah and B.C. Eu, Phys. Rev. Lett. **83**, 4566 (1999); J. Chem. Phys. **114**, 10436 (2001).
[10] K. Rah and B.C. Eu, J. Chem. Phys. **117**, 4386 (2002).
[11] K. Rah and B.C. Eu, J. Chem. Phys. **115**, 2634 (2001).
[12] B.C. Eu and K. Rah, Phys. Rev. E **63**, 031203 (2001).
[13] C.A. Angell, J. Non-Cryst. Solids **102**, 205 (1988).
[14] S. Chapman and T.G. Cowling, *The Mathematical Theory of Nonuniform Gases*, 3rd ed. (Cambridge, London, 1970).
[15] M.H. Cohen and D. Turnbull, J. Chem. Phys. **31**, 1164 (1959).
[16] K. Rah and B.C. Eu, Mol. Phys. **100**, 3281 (2002).
[17] K. Rah and B.C. Eu, Phys. Rev. Lett. **88**, 065901 (2002); J. Chem. Phys. **116**, 7967 (2002).
[18] K. Rah and B.C. Eu (unpublished).
[19] K. Rah and B.C. Eu, J. Phys. Chem. B **107**, 4382 (2003).
[20] *CRC Handbook of Chemistry and Physics*, 79th ed. (CRC Press, Boca Raton, FL, 1999).
[21] J.H. Dymond, *The Second Virial Coefficients of Pure Gases and Mixtures* (Oxford, New York, 1980).
[22] C.A. Angell, J.M. Sare, and E.J. Sare, J. Phys. Chem. **82**, 2622 (1978), and references therein.
[23] A.J. Barlow, J. Lamb, and A.J. Matheson, Proc. R. Soc. London, Ser. A **238**, 322 (1965).
[24] M.J. Assael, N.K. Dalaouti, and J.H. Dymond, Int. J. Thermophys. **21**, 291 (2000).
[25] G.J. Kruger and R. Weiss, Z. Naturforsch. A **25A**, 777 (1970).
[26] G. Hinze and H. Sillescu, J. Chem. Phys. **104**, 314 (1996).
[27] R.J. Greet and D. Turnbull, J. Chem. Phys. **46**, 1243 (1967).
[28] J.N. Andrews and A.R. Ubbelohde, Proc. R. Soc. London, Ser. A **228**, 435 (1955).
[29] M. Cukierman, J.W. Lane, and D.R. Uhlmann, J. Chem. Phys. **59**, 3639 (1973).
[30] W.T. Laughlin and D.R. Uhlmann, J. Phys. Chem. **70**, 2317 (1972).
[31] D.W. McCall, D.C. Douglass, and D.R. Falcone, J. Chem. Phys. **50**, 3839 (1969).
[32] F. Fujara, B. Geil, H. Sillescu, and G. Fleischer, Z. Phys. B: Condens. Matter **88**, 195 (1992).
[33] M.T. Cicerone and M.D. Ediger, J. Chem. Phys. **104**, 7210 (1996).
[34] L.V. Woodcock, Ann. N.Y. Acad. Sci. **371**, 274 (1981).
[35] K. Rah, S. Kwak, B.C. Eu, and M. Lafleur, J. Phys. Chem. A **106**, 11841 (2002).