

## Viscous Flow in Supercooled Liquids Analyzed in Terms of Transport Theory for Random Media with Energetic Disorder

H. Bässler

*Fachbereich Physikalische Chemie, Philipps-Universität, D-3550 Marburg, Federal Republic of Germany*

(Received 9 September 1986)

Viscosity data for supercooled liquids are reexamined in terms of the random-potential model with use of the concept developed for treatment of electronic transport in random media with energetic disorder.  $\eta(T)$  is found to obey the predicted  $\exp[(T_0/T)^2]$  law covering ten decades in  $\eta$  and extending to the glass transition which is considered to be a kinetic localization phenomenon. The crucial system parameter is the width  $\sigma$  of the (Gaussian) distribution of states which determines both the glass transition temperature and the  $T$  dependence of  $\eta$  via the characteristic temperature  $T_0 \propto \sigma$ .

PACS numbers: 51.20.+d, 61.40.+b, 64.70.Pf, 72.80.Ng

When a liquid is cooled it can either crystallize or become supercooled, i.e., remain more or less fluid, until at a certain temperature  $T_g$ , called the glass transition temperature, the viscosity approaches that of an ordinary crystalline solid, albeit without occurrence of crystallization.<sup>1,2</sup> Near  $T_g$  certain thermodynamic variables like the specific volume or entropy exhibit a gradual change in slope rather than in absolute magnitude, suggesting that the transition is not a thermodynamic first-order process. Moreover, the exact value of  $T_g$  depends on the thermal history of the sample although an entropy argument requires the existence of a minimum value for  $T_g$ .<sup>3</sup>

The dramatic increase in viscosity observed upon lowering of the temperature<sup>2,4</sup> is often expressed in terms of the empirical Vogel-Fulcher (VF) relation,<sup>5</sup>  $\eta(T) = A \exp[B/(T - T_g)]$ , although significant deviations are noted as  $T$  approaches  $T_g$ .<sup>6,7</sup> It has been rationalized in terms of the free-volume theory<sup>8-10</sup> which treats the supercooled liquid as a composite of hard spheres and unoccupied space varying linearly with  $T - T_g$ . The latter is thought to provide motional freedom for the liquid particles, required for mechanical flow to occur. The most elaborate version of the free-volume theory is that of Cohen and Grest,<sup>11</sup> who also included the percolative aspect of particle motion. It is conceptually attractive yet does not solve the problems encountered upon analysis of experimental  $\eta(T)$  data. It also predicts the glass transition to be more likely a first-order transition, contrary to experimental evidence.

Following the idea of Goldstein<sup>12</sup> the present Letter advocates treating motional processes in a supercooled liquid near  $T_g$  in terms of a disorder model without invoking the free-volume concept. A characteristic feature of random media is that the physical parameters specifying the state of a structural element, be it a molecule or an atom, are not discrete quantities. Depending on a large number of internal coordinates, each being subject to random yet small amplitude fluctuations, they are realistically modeled by a Gaussian density of states (DOS) function, characterized by its width  $\sigma$ . Experi-

mental signatures are the inhomogeneously broadened absorption profiles of organic glasses testifying to the existence of Gaussian DOS profiles for the electronic energies of the glass-forming molecules,<sup>13,14</sup> and the distribution of tunneling parameters for transitions among two-level systems.<sup>15,16</sup> In the present context the effect of disorder on the migration of an excitation, an electron or a Frenkel exciton generated by photoexcitation, is of particular importance. If initially created at random within the DOS manifold it will be subject to a random-walk process in cause of which it relaxes energetically provided that  $kT \ll \sigma$ . Both Monte Carlo simulation<sup>17</sup> and analytic theory<sup>18,19</sup> predict that in the long-time limit dynamic equilibrium is attained and the diffusion coefficient is expected to obey a characteristic  $D(T) = D_0 \exp[-(T_0/T)^2]$  law. The  $D_0$  is the diffusion coefficient in the energetically discrete counterpart structure and  $T_0$  is related to  $\sigma$  by  $kT_0 = 0.64\sigma$ .<sup>18</sup> A simple thermodynamic argument<sup>19</sup> predicts that the mean energy relative to the center of the DOS, at which a hopping particle equilibrates in the  $t \rightarrow \infty$  limit, is  $\langle \epsilon_\infty \rangle = -\sigma^2/kT$ . This functional form of  $\epsilon_\infty(T)$  reflects the interplay between thermal excitation and relaxation and is specific for a Gaussian DOS yet is virtually independent of details of the transport process, notably the nature of the intersite coupling potential. It explains why the  $T$  dependence of  $D_\infty$  deviates from an Arrhenius behavior. Since  $\epsilon_\infty$  decays as  $T^{-1}$ , the mean activation energy required for an excitation to jump to a neighbor site increases accordingly. Experimental work on both exciton<sup>20</sup> and charge transport studies<sup>21</sup> on random organic systems below  $T_g$  support this concept.

Excitation-transport theory for random media has thus provided the framework for treating relaxation as well as motion of particles in a random potential quantitatively, provided that the potential fluctuations can be considered static on the time scale of an elementary hopping process. Bearing in mind that the statistical variation of the intermolecular coordinates in a supercooled liquid generates a multidimensional potential energy surface with

local maxima and minima, realistically approximated by a Gaussian DOS, it appears attractive to adapt the above model to viscous flow also, considering, however, that the potential distribution is different from that governing electronic transport. One has to assume that upon cooling, the glass-forming molecules become localized in the deeper states of the DOS and—critically—that the overall temporal variation of the DOS is slow. The latter postulate is likely to be fulfilled at temperatures near  $T_g$  where the fraction of molecules undergoing thermally activated transitions is small thus ensuring that an individual jump occurs within a virtually constant potential. After a time sufficient for the particles to equilibrate at a mean energy  $\langle \epsilon_\infty \rangle = -\sigma^2/kT$  within the DOS transitions among adjacent potential minima occur at an average rate  $\langle \nu \rangle \sim \exp[-(T_0/T)^2]$ . Supposing that viscosity scales inversely with the rate of thermal excitations within the random potential, we have

$$\eta(T) = \eta_\infty \exp[(T_0/T_0)^2], \quad (1)$$

expected for  $T > T_g$ .

With this concept in mind I reanalyzed existing viscosity data for a number of glasses, both inorganic and organic. Figure 1 presents a representative selection of  $\eta(T)$  data plotted on a  $\log \eta$  vs  $T^{-2}$  scale. It is obvious (i) that Eq. (1) fits experimental data over typically ten

orders of magnitude remarkably well, including the high-viscosity regime where the VF law notoriously overestimates freezing in of viscous flow, and (ii) that two categories of glasses exist distinguished by a deviation from Eq. (1) for  $\log \eta < 3 \pm 1$ . Figure 1 suggests that previous identification of an Arrhenius type of  $T$  dependence near  $T_g$ , albeit with the recognition of a slight curvature in slope,<sup>4,5</sup> is accidental and is caused by the similarity of  $\log \eta$  vs  $T^{-1}$  and vs  $T^{-2}$  plots if confined to a narrow temperature regime. The behavior implied by Eq. (1) is also revealed in the temperature dependences of dielectric relaxation<sup>2,22</sup> and frequency-dependent specific heat<sup>23</sup> (Fig. 2). It is noteworthy that the  $T_0$  values inferred from the three categories of observables available for glycerol are identical, demonstrating that the slow relaxational modes governing time-dependent uptake of heat also control momentum transfer processes involved in viscous flow and, concomitantly, dipole relaxation. While difficult to rationalize in terms of the free-volume concept this appears to be a plausible consequence of a random potential model that considers small-amplitude displacements of the structure elements, or segments thereof, as the elementary excitations. On the other hand, the weak dependence of the thermal conductivity on  $T$ <sup>23</sup> indicates that these excitations are unimportant in heat flow.

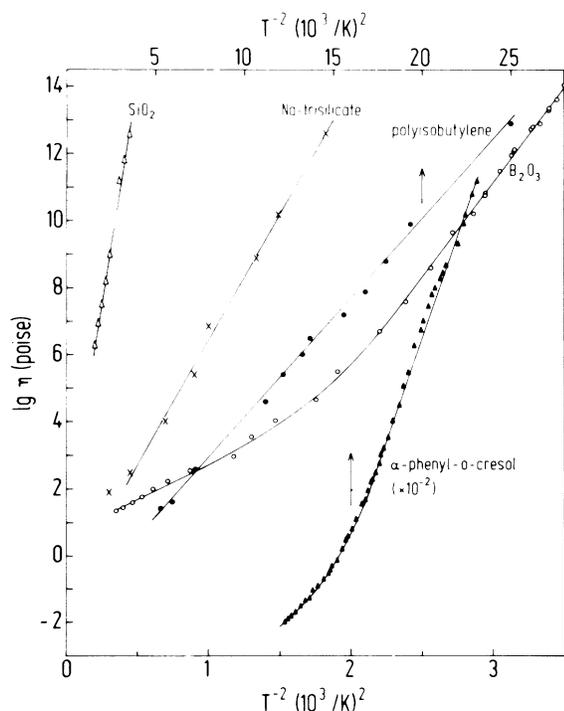


FIG. 1. Temperature dependence of the viscosity of various supercooled liquids plotted on a  $\log \eta$  vs  $T^{-2}$  scale. Data for  $B_2O_3$  and  $\alpha$ -phenyl-*o*-cresol are from Refs. 6 and 7, respectively; the remaining data are from Refs. 2 and 4.

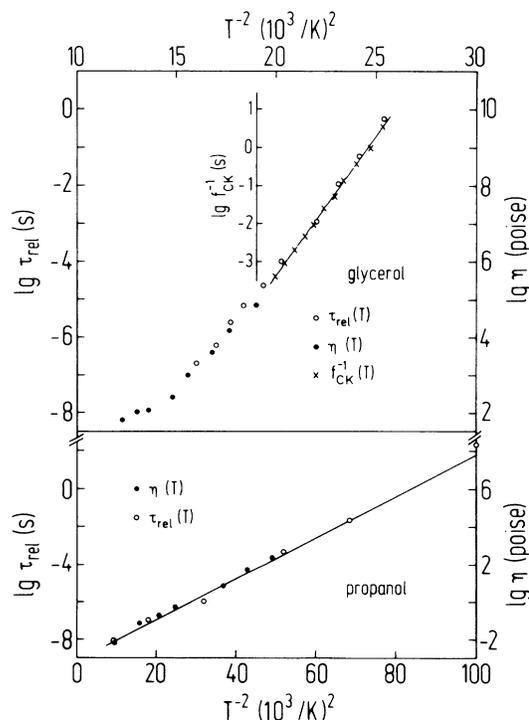


FIG. 2. Comparison of the  $T$  dependences of  $\eta$  (Ref. 4) and dielectric relaxation time (Refs. 2 and 3) for propanol and glycerol.  $f_{C\kappa}$  is the peak frequency of the imaginary part of the product of specific heat and thermal conductivity (Ref. 24).

Figure 3 compiles  $T_0$  data determined from the linear segments of  $\log \eta$  vs  $T^{-2}$  plots for a series of glasses as a function of  $T_g$  and demonstrates that both quantities are related. Two groups of data points can be distinguished, both bearing a linear relationship  $T_0 = CT_g$  yet with different proportionality constants. The four monomeric organic substances and the ionic salt  $4\text{Cs}(\text{NO}_3)_2 \cdot 6\text{KNO}_3$ , referred to as group 1, yield  $C = 9.25 \pm 0.15$ ; the inorganic glasses, the polymer polyisobutylene, and propanol and glycerol which both form intermolecular hydrogen bonds (group 2) give  $C = 6.0 \pm 0.5$ .

Since  $T_g$  agrees with the temperature at which  $\eta$  approaches the value characteristic of a crystalline solid ( $\approx 10^{13}$ – $10^{14}$  P), one can relate the pre-exponential factor  $\eta_\infty$  to  $T_g$  and rewrite Eq. (1) in the normalized form  $\eta = 10^{14} \exp[(T_0/T)^2 - (T_0/T_g)^2]$  P. The correlation between  $\eta_\infty$  and  $T_g$ ,  $\eta_\infty = 10^{14} \exp[-(T_0/T_g)^2] = 10^{14} \times \exp(-C^2)$  P, is the equivalent of the entropy-enthalpy relation often observed with conventional chemical reactions. For glasses belonging to groups 1 and 2, respectively,  $\log \eta_\infty = -23 \pm 1$  and  $-1.5 \pm 1.5$  is obtained. While Eq. (1) is universally obeyed for all glasses in the high-viscosity regime,  $\eta(T)$  of group-1 glasses begins to level off at  $T \approx \frac{3}{4} T_g$ , equivalent to  $\log \eta = 3 \pm 1$ , and approaches  $\log \eta \sim -1$  at the melting temperature  $T_m \approx \frac{3}{2} T_g$ .<sup>2</sup> Equation (1) must fail once thermally excited motion of the structure elements of the glass become fast enough to invalidate the underlying concept of a quasi-static DOS. The disorder affecting an individual segmental motion is then smeared out temporarily. This is equivalent to a temperature-induced reduction of the width of the DOS which translates into a reduction of  $T_0$  in Eq. (1). At present no firm explanation can be given why group-1 glasses exhibit this effect at lower reduced temperatures  $T/T_g$  than group-2 glasses. It is, however, noteworthy that group-1 glasses do not form intermolecular networks while group-2 glasses do. Lack of inter-

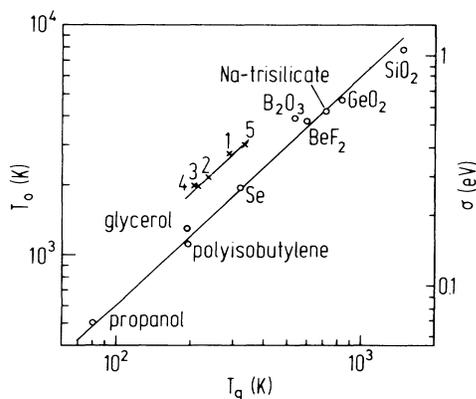


FIG. 3. Correlation between  $T_0$  defined via Eq. (1) and  $T_g$  for various supercooled liquids. 1, glucose; 2, *o*-terphenyl; 3,  $\alpha$ -phenyl-*o*-cresol; 4, salol; 5,  $4\text{Ca}(\text{NO}_3)_2 \cdot 6\text{KNO}_3$ .  $\sigma$  is the Gaussian width of the DOS.

molecular directional bonds is expected to facilitate molecular displacement and the formation of free volume. Interestingly, the low- $\eta$  regime of those systems is well described by either VF with a divergence temperature  $> T_g$  or by more sophisticated treatments taking into account the cooperative nature of flow on a microscopic scale.<sup>25</sup> The latter predict that  $\mu(T)$  scales with  $(T - T'_0)$ . However, the experimental  $T'_0$  turns out to be  $> T_g$ <sup>24</sup> demonstrating that the high-viscosity regime is not recovered.

It is of interest to compare  $\sigma$  values indicated in Fig. 3 with the heat of sublimation per molecule which may be taken as an estimate for the binding energy of the molecule in the structure. In the sequence propanol, glycerol, glucose, and Se,  $\sigma/\Delta H$  values are 0.15, 0.18, 0.25, and 0.28, respectively. Fluctuation of the potential energies of the glass-forming elements of order 20% of the total binding energy appears realistic. It is comparable to the relative spread of other quantities like the gas to solid shift of optical transitions<sup>13</sup> in organic molecular solids.

Additional support for the proposed model comes from an entropy consideration. Figure 4 reproduces the entropy difference between the supercooled liquid and the solid state of lithium acetate on a  $\Delta S$  vs  $T^{-2}$  scale.<sup>2</sup> The data points fall on a straight line, demonstrating that  $S_1 - S_{\text{cryst}} \sim T_g^{-2} - T^{-2}$ . This functional form is recovered if one considers the increase in the thermodynamic probability function for an ensemble of particles equilibrated within a Gaussian DOS. As the temperature is raised from  $T_g$  to  $T$  the mean energy of the ensemble increases from  $\langle \epsilon(T_g) \rangle = -\sigma^2/kT_g$  to  $\langle \epsilon(T) \rangle = -\sigma^2/kT$ , relative to the center of the DOS. Concomitantly, the distribution of states  $g(T)$  available for the particles also changes according to

$$g(T) = N(2\pi)^{-1} \int_{-\infty}^{\langle \epsilon(T) \rangle / \sigma} \exp(\epsilon'^2 / 2\sigma^2) d(\epsilon'/\sigma),$$

where  $N$  is the total number of states. Since

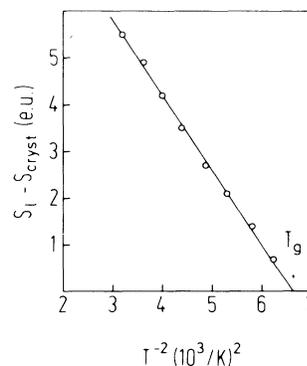


FIG. 4. Difference in entropy between liquid and crystalline phases for lithium acetate as a function of  $T^{-2}$  (data are from Ref. 2).  $T_g$  is the extrapolated "ideal" glass transition temperature.

$(\langle \epsilon \rangle / \sigma)^2 = (\sigma / kT)^2 \ll 1$ , the integral is approximately proportional to  $\exp[-\epsilon^2 / \sqrt{2}\sigma^2]$ . Taking into account that  $\sigma/k = T_0/0.64$  (see above), one finds that the increase in entropy between  $T_g$  and  $T$  should approximately be

$$S(T) - S(T_g) \cong kN \ln[g(T)/g(T_g)] \\ \cong 2^{-1/2} kN (\sigma/k)^2 (1/T_g^2 - 1/T^2).$$

A quantitative estimate would require knowledge of the partition function.

The model advanced above implies that the glass transition in a supercooled liquid is a kinetic localization phenomenon rather than a thermodynamic phase transition. This explains why thermodynamic functions vary rather smoothly near  $T_g$  contrary to what is expected in case of a phase transition. The crucial quantity that determines both  $T_g$  and the rate at which  $\eta$  varies with temperature is the width of the density of states which is a measure of the frozen-in potential distribution. A logical consequence is the dependence of  $T_g$  on sample history because the DOS profile and its occupation depend on preparation conditions.

Helpful conversations with Professor S. Grossman, Professor J. Stuke, and Dr. R. Richert are gratefully acknowledged. This work has been carried out as part of a research program sponsored by the Deutsche Forschungsgemeinschaft.

<sup>1</sup>See, e.g., S. R. Elliot, *Physics of Amorphous Materials* (Longman, London, 1983).

<sup>2</sup>J. Wong and C. A. Angell, *Glass Structure by Spectroscopy* (Marcel Dekker, New York, 1976).

<sup>3</sup>W. Kauzmann, *Chem. Rev.* **43**, 219 (1948).

<sup>4</sup>*Die Physik der Hochpolymeren*, edited by H. A. Stuart (Springer-Verlag, Berlin, 1955); see also E. Jenckel, *Z. Phys. Chem. A* **184**, 309 (1939).

<sup>5</sup>G. S. Fulcher, *J. Am. Ceram. Soc.* **8**, 339 (1925).

<sup>6</sup>P. B. Macedo and A. Napolitano, *J. Chem. Phys.* **49**, 1887 (1968).

<sup>7</sup>W. T. Laughlin and D. R. Uhlmann, *J. Phys. Chem.* **76**, 2317 (1972).

<sup>8</sup>A. K. Doolittle, *J. Appl. Phys.* **22**, 1031 (1981).

<sup>9</sup>M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.* **77**, 3701 (1953).

<sup>10</sup>M. H. Cohen and D. Turnbull, *J. Chem. Phys.* **31**, 1164 (1959).

<sup>11</sup>M. H. Cohen and G. S. Grest, *Phys. Rev. B* **20**, 1077 (1979).

<sup>12</sup>M. Goldstein, *J. Chem. Phys.* **51**, 3728 (1969).

<sup>13</sup>R. Jankowiak, K. Rockwitz, and H. Bässler, *J. Phys. Chem.* **87**, 552 (1983).

<sup>14</sup>J. Friedrich and D. Haarer, *Angew. Chem.* **96**, 96 (1984).

<sup>15</sup>R. Jankowiak, R. Richert, and H. Bässler, *J. Phys. Chem.* **89**, 4569 (1985).

<sup>16</sup>R. Jankowiak and G. J. Small, *Chem. Phys. Lett.* **128**, 377 (1986).

<sup>17</sup>G. Schönherr, H. Bässler, and M. Silver, *Philos. Mag. B* **44**, 369 (1981).

<sup>18</sup>M. Grünewald, B. Pohlmann, B. Movaghar, and D. Würtz, *Philos. Mag. B* **49**, 341 (1984).

<sup>19</sup>B. Movaghar, M. Grünewald, B. Ries, H. Bässler, and D. Würtz, *Phys. Rev. B* **33**, 5545 (1986).

<sup>20</sup>R. Richert and H. Bässler, *J. Chem. Phys.* **84**, 3567 (1986).

<sup>21</sup>H. Bässler, G. Schönherr, M. Abkowitz, and D. Pai, *Phys. Rev. B* **26**, 3105 (1982).

<sup>22</sup>C. A. Angell and D. L. Smith, *J. Phys. Chem.* **86**, 3845 (1982).

<sup>23</sup>N. O. Birge, *Phys. Rev. B* **34**, 1631 (1986).

<sup>24</sup>P. Taborek, R. N. Kleiman, and D. J. Bishop, *Phys. Rev. B* **34**, 1835 (1986).

<sup>25</sup>U. Bengtzelius, W. Götze, and A. Sjölander, *J. Phys. C* **17**, 5915 (1984).