Low-Temperature Relaxation and Entropic Barriers in Supercooled Liquids

Udayan Mohanty, Irwin Oppenheim, Clifford H. Taubes

The low-temperature relaxation dynamics of supercooled liquids are a long-standing theoretical problem of considerable interest. The vast amount of experimental data on such liquids indicates that viscosity and diffusion in supercooled liquids are non-Arrhenius over a wide range of temperatures. The non-Arrhenius temperature dependence of the relaxation time of the slow modes in glass-forming liquids is investigated in connection with the topology of the potential energy landscape in configuration space. An analogy is made between the derived dynamical equations and Cooper's formulation of the pair equation in superconductivity.

Although our understanding of the dynamics and equilibrium properties of liquids has increased dramatically over the past two decades, the low-temperature relaxation dynamics of glass-forming liquids are a fundamental and major unsolved problem. Liquids can be supercooled under appropriate conditions of pressure and temperature. A supercooled liquid is dynamically metastable because a small perturbation may result in a transition to the crystalline state. A vast amount of experimental data indicates that supercooled states are characterized by universal features (*1–5*): (i) The viscosity of glass-forming liquids as a function of temperature shows deviations from Arrhenius behavior and is described (*3*, *4*) by the Vogel-Tammann-Fulcher or the Williams-Landel-Ferry laws (Fig. 1). (ii) The frequency dependence of shear viscosity and dielectric relaxation are well accounted for by the Barlow-Erginsav-Lamb or the Cole-Cole relations (*1*, *2*). (iii) The observed secondary relaxation (*5*) is an intrinsic property of the metastable equilibrium liquid above the glass transition temperature T_g (*6*) and is a result of localized molecular motions.

The dynamics of liquids have been studied by various researchers by the inherent structure approach to condensed phases (*2*, *7–12*). In this approach, one separates the mechanically stable packing configurations, which correspond to the local minima in the potential energy surface, from anharmonic vibrations about these molecular packings. The inherent structure approach provides a tool for investigating the slow and the fast relaxation modes observed in glass-forming liquids (Fig. 2). In this report, we synthesize the inherent structure approach with nonequilibrium statistical mechanical techniques to investigate how the relaxation time for the slow configurational modes is connected with the topology of the potential energy landscape in configuration space. In fact, Frauenfelder *et al.* (*13*) have studied how these complex landscapes of glasses and spin glasses are related to dynamical motion in proteins.

We consider a classical system of N particles interacting with a potential $\Phi(\mathbf{r})$. The coordinates of all the particles are denoted by $\mathbf{r}$. The configuration space Γ of a supercooled liquid excludes crystalline packings. The various minima in $\Phi(\mathbf{r})$ and its distribution, in glass-forming liquids, can be identified at least in principle (Fig. 2) by suitable projections (*2*, *12*). We characterize the potential surface by a collection of intensive order parameters $\{\xi_\alpha\}$ (*12*). In the thermodynamic limit, the density of minima in the order-parameter space is proportional to $\exp[\sigma(\xi_\alpha)N]$, where $\sigma(\xi_\alpha)$ is proportional to the configurational entropy per particle (*12*). The basins of these minima define a set of disjoint cells that span the configuration space (*2*, *14*). The cells are described by a characteristic function $C_\alpha(\Gamma)$, whose value is unity if the position in configuration space, Γ, is in cell α and zero otherwise (*2*, *14*).

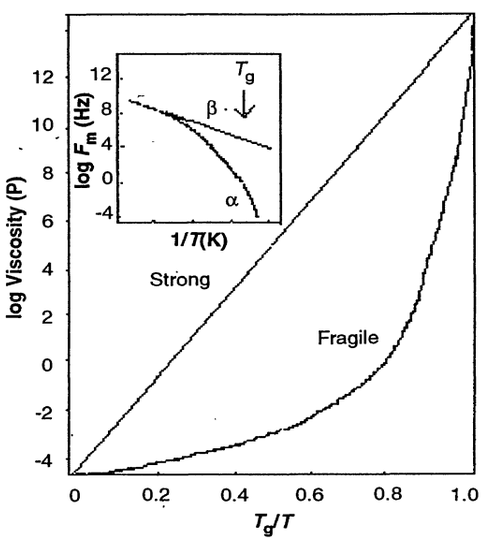

Fig. 1. A sketch of the temperature dependence of the relaxation time $\tau(T)$ [related to viscosity in poise (1 P = 1 dyne · s cm^{-2})] for strong and fragile glass-forming liquids (*4*). For fragile liquids, $\tau(T)$ is described by the Vogel-Tammann-Fulcher relation—namely, $\tau(T) = A \exp D_0/(T - T_0)$—over twelve orders of magnitude in variations in the relaxation time, provided T_0 is close to the Kauzmann temperature T_k; A and D_0 are empirical parameters. (**Inset**) A sketch of the temperature dependence of dielectric relaxation rates (F_m) of main (α) and secondary (β) relaxations (*4*, *5*). At $T_x \approx 1.3\ T_g$, the α and β relaxations bifurcate (*4*, *5*).

The time dependence of the probability of a state point to be in a cell α at time t, $P_\alpha(t)$, in configuration space is obtained by the use of projection operator techniques (*2*, *14*). If we assume that the memory of the initial cell is lost, then the time dependence of the residence probabilities in a cell α is governed by a master equation, in which the transition probabilities satisfy detailed balance (*14*, *15*). At low temperatures, there is a large number of independent but localized rearranging regions in the sample, and rearrangements in each region involve only a small (of order unity) subset of particles (*2*, *8*, *11*, *12*). Consequently, a van Kampen system size expansion (*12*, *15*) leads, in the continuum limit, to a Fokker-Planck equation in the order-parameter space (*16*).

$$\frac{dP(\xi,E;t)}{dt} = -\nabla\cdot[(\zeta\cdot\mathbf{F})P(\xi,E;t)] + \frac{1}{\beta}\nabla\cdot[\zeta\cdot\nabla P(\xi,E;t)] \qquad (1a)$$

where the diffusion coefficient D (tensor) in the order parameter space is related to the mobility $\zeta(\xi, E)$ by means of $D(\xi, E) = k_B T\ \zeta(\xi, E)$, where $\beta = 1/k_B T$ and k_B is the Boltzmann constant. Note that the thermodynamic force $\mathbf{F}$

$$\mathbf{F}(\xi,E) = (k_B\beta)^{-1}\nabla S(\xi,E) \qquad (1b)$$

appearing in Eq. 1a is the result of entropic "barriers" (*2*, *12*, *17*). The configurational entropy at energy E is denoted by $S(\xi_\alpha, E)$ and is related to $\sigma(\xi_\alpha)$ (*2*, *12*).

Classical nucleation theory (*1*) predicts that if thermal fluctuations were such that the droplet size or the size of a cooperative rearranging region (*18*) is larger than a critical value, then the system lowers its free energy by crystallization. In this sense, the subset of order parameters $\xi^f = \xi^f(E)$, for which the free energy $F(\xi)$ is an extremum, describes a critical droplet. The surface where $\nabla S(\xi, E)$ vanishes defines a constraint $\xi^s = \xi^s(E)$. Our viewpoint is that the non-Arrhenius rate processes observed in glass-forming liquids arise from the relaxation toward equilibrium of the slow mode on $\xi^* = \xi^*(E)$, which is the intersection of ξ^f with ξ^s.

U. Mohanty, Eugene F. Merkert Chemistry Center, Department of Chemistry, Boston College, Chestnut Hill, MA 02167, USA.
I. Oppenheim, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.
C. H. Taubes, Department of Mathematics, Harvard University, Cambridge, MA 02138, USA.

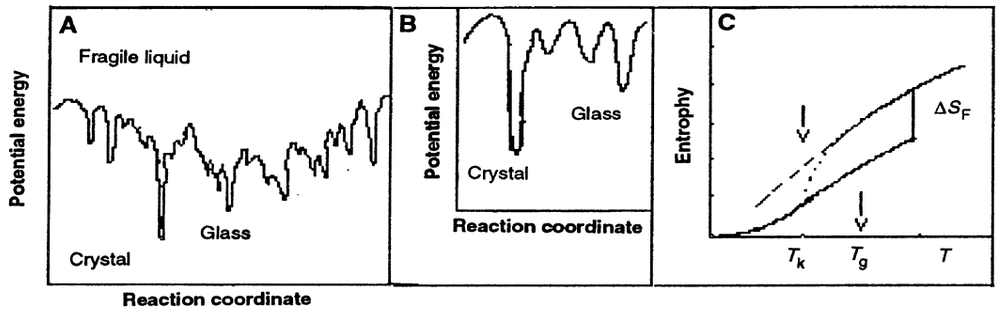

Fig. 2. A sketch of the potential energy landscape of (**A**) fragile and (**B**) strong glass-forming liquids viewed along a one-dimensional reaction coordinate (*4*). The potential energy landscape for fragile liquids has a large number of local minima of various depths. The situation is similar to proteins and spin glass (*13*). (**C**) The entropy of a supercooled liquid as a function of temperature. The dashed and the dotted lines represent an extrapolation of the entropy of strong and fragile liquids, respectively. At T_k, the entropy of a supercooled liquid is equal to the entropy of the corresponding crystalline phase. ΔS_F is the entropy of fusion.

It is fruitful to introduce the curvature (Fig. 3) of the entropic barriers $\kappa_{s;np}(\xi, E)$ defined as $\{\partial^2[S(\xi, E)/k_B]/\partial\xi_n\partial\xi_p\}$. On expanding $P(\xi, E; t)$ as $\Sigma_n a_n \psi_n(\xi, E) \exp(-\omega_n t)$, one obtains from Eq. 1

$$[D^*(E)\Sigma_\ell k_\ell^2 - \omega_n]\Phi_n(k,E) = \{[V_\xi/(2\pi)^d]D^*(E) \Sigma_\ell T_{s;\ell\ell}(k^*;E)\}\int \Phi_n(k',E)d^dk' \quad (2)$$

Here, d is the dimension of the order parameter space of volume V_ξ, and $\Phi_n(k, E)$ and $T_{s;\ell\ell}(k, E)$ are the Fourier transforms of $\psi_n(\xi, E)$ and $\kappa_{s;np}(\xi, E)$, respectively. In deriving Eq. 2, we have assumed that the curvature of the entropic barrier is parallel to the diffusion tensor, the latter being replaced by its average value $D^*(E)$ on $\xi^*(E)$, and $T_{s;\ell\ell}(k - k', E)$ is approximated (*19*) by $T_{s;\ell\ell}(k^*; E)$, where $k^*\cdot\xi^* \approx (2\pi)^d$.

Observe that Eq. 2 is identical in form to the Cooper pair equation in superconductivity (*20*). The diffusion coefficient $D^*(E)$ plays the same role as the inverse reduced mass of a pair of electrons. The parameters $\Phi_n(k, E)$ and $T_{s;\ell\ell}(k^*; E)$ are analogous to the wave function and an attractive interaction between the Cooper pair in momentum representation, respectively.

The integral equation can be explicitly solved along the lines pioneered by Cooper (*20*). Let us denote the right side of Eq. 2 by $\Lambda(E)$. Then, $\Phi_n(k, E)$ is given by $1/[D^*(E)\Sigma_\ell k_\ell^2 - \omega_n]\Lambda(E)$. Substituting this expression for $\Phi_n(k, E)$ back in the right side of Eq. 2 leads to

$$1 = \frac{V_\xi}{(2\pi)^d}\Sigma_\ell T_{s;\ell\ell}(k^*;E) \int d^dk'/[\Sigma_\ell k_\ell^2 - \omega_n/D^*(E)] \quad (3)$$

Experiments indicate that at least two order parameters are required to describe the supercooled and glassy states (*21*). In this case (*22*), the integrals can be evaluated. The temperature dependence of the relaxation time of the slow mode, $\tau_s(T)$, is non-Arrhenius

$$\tau_s(T) \approx \tau_D \exp[B/TS(k^*,E)] \quad (4)$$

and governed primarily by the configurational entropy of the supercooled liquid. Both τ_D and B are functions of the order parameters and are temperature dependent (*23*). If $S(k^*, E)$ is approximated (*24*) as the product $S(E)f(k^*)$, then $\tau_s(T)$ is of the form suggested by Adam and Gibbs (*18*).

In glass-forming liquids, the configuration heat capacity change at constant pressure, ΔC_p, is well approximated by A_0/T, where A_0 is a constant (*2*, *4*, *25*). This then leads to the identity of the Kauzmann temperature T_k and the temperature T_0 at which the configurational entropy vanishes (*2*, *4*, *24*). Thus, $\tau_s(T)$ is nonanalytic as $T \rightarrow T_k$ (Fig. 1), as suggested by the Vogel-Tammann-Fulcher relation (*1*–*4*). This is reminiscent of the nonanalytic dependence of the binding energy Δ of a Cooper pair on the strength of the attractive interaction χ (*20*)

$$\Delta \approx k_B\theta_D \exp[-1/\chi\rho(\varepsilon_f)] \quad (5)$$

where $\rho(\varepsilon_f)$ is the density of states of the electrons at the Fermi energy ε_f, and θ_D is the Debye temperature (*26*). In both cases, nonanalyticity cannot be obtained by perturbation calculation.

Our results are in accord with experiments which show that the temperature dependence of configurational slow modes, which decouple from the viscous modes, is non-Arrhenius (*4*). Thus, our approximation with finitely many order parameters may be justified (*22*). Examples of order parameters include volume per particle, distribution of coordination numbers, and depth of minima per particle (*12*). A complete set of order parameters is required to describe all relaxation modes that are measurable. Thus, the choice of order parameters is governed by the nature of the physical application in relation to measurable quantities in an experiment. A quantity such as the vibrational partition function is not sensitive to order-parameter variations (*12*). This is so because for $T < T_g$, the vibrational heat capacity of glasses and the corresponding crystalline solid are similar (*27*).

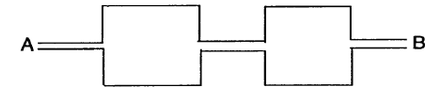

Fig. 3. A two-dimensional view of an entropic channel along appropriate reaction coordinates. The channels do not have potential barriers. The time to traverse from A to B by means of Brownian motion depends on the topology of the bulges as well as on the constrictions.

The number of unstable modes f_u is an indicator of the fluidity of the system (*28*, *29*). It indicates the number of directions away from a barrier region. One therefore anticipates a connection between the self-diffusion coefficient and f_u (*28*, *29*). The quantity f_u determines the time spent on the peaks (*29*). The ratio of the time spent in a valley, τ_v, to the time spent in crossing a barrier, τ_b, is therefore proportional to $(1 - f_u)/f_u$ and hence to the self-diffusion coefficient D (*2*, *11*, *29*). The formalism developed here allows us to calculate the diffusion coefficient and a crossover temperature in terms of stable and unstable modes (*30*). The formulation may elucidate (*30*) the bifurcation and the temperature dependence of the "slow" β relaxations (*5*) and why the ultrafast orientational dynamics of side groups in a variety of systems are independent of temperature over a wide range of η/T, where η is the shear viscosity (*31*).

REFERENCES AND NOTES

1. J. Jackle, *Rep. Prog. Phys.* **49**, 171 (1986); G. Harrison, *The Dynamical Properties of Supercooled Liquids* (Academic Press, New York, 1976).
2. For a recent review, see U. Mohanty, in *Advances in Chemical Physics*, vol. 89, I. Prigogine and S. A. Rice, Eds. (Wiley, New York, 1994), chap. 2.
3. M. Williams, R. Landel, J. Ferry, *J. Am. Chem. Soc.* **77**, 3701 (1955); H. Vogel, *Phys. Z.* **22**, 645 (1921); G. Tammann and G. Hesse, *Z. Anorg. Allg. Chem.* **156**, 245 (1926).
4. C. A. Angell, *J. Phys. Chem. Solids* **49**, 863 (1988); *J. Non-Cryst. Solids* **102**, 205 (1988).
5. G. P. Johari, in *Relaxations in Complex Systems*, K. L. Ngai and G. B. Wright, Eds. (National Technical Information Service, U.S. Department of Commerce, Springfield, VA, 1985), p. 3.
6. The quantity T_g is the temperature at which the shear viscosity is 10^{13} P.
7. T. A. Weber and F. H. Stillinger, *Phys. Rev. B* **32**, 5402 (1985).
8. M. Goldstein, *J. Chem. Phys.* **51**, 3728 (1969).
9. H. Jonsson and H. C. Andersen, *Phys. Rev. Lett.* **60**, 2295 (1988).
10. M. Ruiz, U. Mohanty, J. Brey, *J. Chem. Phys.* **99**, 9979 (1993).
11. R. Zwanzig, *ibid.* **79**, 4507 (1983); U. Mohanty, *Phys. Rev. A* **32**, 3055 (1985); *J. Chem. Phys.* **89**, 3778 (1988).
12. F. H. Stillinger, *Phys. Rev. B* **41**, 2409 (1990).
13. H. Frauenfelder, S. G. Sligar, P. G. Wolynes, *Science* **254**, 1598 (1991).
14. R. Zwanzig, *J. Stat. Phys.* **30**, 255 (1983); U. Mo-

hanty, *Phys. Rev. A* **34**, 4993 (1986).
15. N. G. van Kampen, *Stochastic Process in Physics and Chemistry* (North-Holland, Amsterdam, 1981).
16. $P(\xi_\alpha, t) = \exp[N\sigma(\xi_\alpha)]P_\alpha(t)$.
17. M. Fixman, *J. Chem. Phys.* **69**, 1527 (1978); R. Zwanzig, *J. Phys. Chem.* **96**, 3926 (1992).
18. G. Adam and J. H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965); U. Mohanty, *Physica A* **162**, 362 (1990); T. Kirkpatrick, D. Thirumalai, P. G. Wolynes, *Phys. Rev. A.* **40**, 1045 (1989).
19. $T_{s;\epsilon\epsilon}(k - k'; E)$ is nonzero in the range $k^* + dk^* < k' < k^*$. The assumption that the curvature is the parallel to the diffusion tensor is adopted to simplify presentation. This assumption can be removed.
20. L. Cooper, *Phys. Rev.* **104**, 1189 (1956).
21. G. W. Scherer, *Relaxation in Glass and Composites* (Wiley, New York, 1986).
22. Our results can be generalized to an arbitrary number of order parameters (*30*).
23. To simplify presentation, the expressions for τ_D and B have not been included; see (*22*).
24. This defines the function $f(k^*)$. In the Adam-Gibbs relation, the relaxation time of a rearranging region is of the form $\tau \approx \tau_0 \exp(C/Ts)$, where C is weakly temperature dependent. Here, s is the configurational entropy that excludes vibrational degrees of freedom.
25. C. A. Angell and W. Sichina, *Ann. N.Y. Acad. Sci.* **279**, 53 (1976); V. P. Privalko, *J. Phys. Chem.* **84**, 3307 (1980).
26. S. Doniach and E. H. Sondheimer, *Green's Functions for Solid State Physicists* (Benjamin, New York, 1974).
27. See, for example, S. S. Chang and A. B. Bestul, *J. Chem. Phys.* **56**, 503 (1972).
28. R. Cotterill and J. Madsen, *Phys. Rev. B* **33**, 262 (1986).
29. G. Seeley, T. Keyes, B. Madan, *J. Chem. Phys.* **95**, 3847 (1991).
30. U. Mohanty, I. Oppenheim, C. H. Taubes, unpublished results.
31. A. Sengupta and M. D. Fayer, *J. Chem. Phys.* **100**, 1673 (1994).
32. U.M. thanks S. Rice, M. Fixman, and R. Marcus for their encouragement over the years during which this research was carried out.

8 July 1994; accepted 1 September 1994

Surface-Skimming Stoneflies: A Possible Intermediate Stage in Insect Flight Evolution

James H. Marden* and Melissa G. Kramer

Insect wings appear to have evolved from gills used by aquatic forms for ventilation and swimming, yet the nature of intermediate stages remains a mystery. Here a form of nonflying aerodynamic locomotion used by aquatic insects is described, called surface skimming, in which thrust is provided by wing flapping while continuous contact with the water removes the need for total aerodynamic weight support. Stoneflies surface skim with wing areas and muscle power output severely reduced, which indicates that surface skimming could have been an effective form of locomotion for ancestral aquatic insects with small protowings and low muscle power output.

Insects evolved the ability to fly approximately 330 to 400 million years ago, and they subsequently radiated and diversified to become the most speciose life form on the planet (*1*). How flight evolved in insects has been a topic of frequent debate (*2*), because the answer may yield valuable insight into reasons for insect diversification. Furthermore, flight exemplifies one of the great challenges for evolutionary biology, which is to determine transitions in function and selective advantage for intermediate stages during evolution of complex suites of interdependent anatomical, physiological, and behavioral features (*3*).

Fossils offer tantalizing clues regarding morphology and skeletal anatomy of certain primitive insect fliers (*4*); however, the fossil record is too sparse to resolve key phylogenetic or functional transitions. Recent debate has focused predominantly on the anatomical origin of wings (immovable thoracic lobes or articulated gills) and whether small protowings served originally for adaptive aerodynamic functions (*5*) or were used for thermoregulation and only subsequently became adapted for flight (*6*). Presently, the fossil, neurological, and developmental evidence (*4*, *7*) favors the wings-from-gills model (*2*); however, no previous hypotheses have offered a detailed model explaining how fliers could have evolved from swimmers, nor have they utilized detailed examinations of behavior, physiology, and morphology of the extant insect orders (Ephemeroptera and Plecoptera) that are anatomically and phylogenetically closest to preflight fossil insects.

Surface skimming, a wing-flapping mode of locomotion used by certain adult stoneflies (Plecoptera) and subadult mayflies (Ephemeroptera), is an attractive candidate for an intermediate stage between swimming and flying. Surface skimming consists of planar movement across a water surface, wherein propulsion is supplied by aerodynamic thrust, while continuous contact with the water removes the need for total aerodynamic weight support (Fig. 1). Thus, all components of the flight motor (wings, wing articulations, muscles, and neuromotor patterns) of primitive surface skimmers could have simultaneously undergone selection for incremental improvement in flapping aerodynamic performance. Here we present an experimental test of the hypothesis that incremental increases in wing size, flight musculature, and muscle power output bring about incremental improvement in the surface-skimming performance of a stonefly.

Stoneflies are weak-flying or nonflying aquatic insects that, except for wings, show relatively little morphological divergence from fossil ancestors dating back to the Carboniferous (Fig. 2) (*8*). *Taeniopteryx burksi* (Plecoptera: Taeniopterygidae) is a winter-emerging stonefly that is common across eastern and central North America, whose only conspicuous use of wing flapping in the field is for surface skimming (Fig. 1). In central Pennsylvania during February and March, *T. burksi* adults emerge and use surface skimming to cross open water whenever they emerge at a distance from shore (on emergent mid-stream rocks, sticks, or ice). After exiting the stream, adults feed terrestrially and arboreally on algae, and they mate (*9*). We have observed thousands of individuals in the field (ambient temperature 0° to 12°C) but have never seen one fly.

We videotaped surface-skimming locomotion of normal and wing-clipped individuals in the lab to determine how skimming velocity is affected by relative wing size, flight muscle ratio (the ratio of thoracic muscle mass to total body mass, a strong determinant of performance in flying insects) (*10*), temperature (which affects muscle power output in ectotherms) (*11*), and body size (*12*). Skimming velocity increased in a continuous, incremental fashion with increasing temperature, relative wing area, and flight muscle ratio (Table 1 and Fig. 3), reaching speeds as high as 44 cm/s. Surface skimming was effective even at temperatures as low as 1.5°C (Fig. 3), when muscle power output of ectothermic insects is severely restricted (*11*, *13*), and with wing size reduced to as little as 20 to 30% of normal (Figs. 1C and 4).

Unlike their behavior at cold ambient temperatures in the field, most *T. burksi* adults do attempt to fly in the lab (air temperature = 22°C). We classified performance of 31 flight-willing individuals as either (i) able to gain altitude in a sustainable fashion, (ii) able to sustain only level flight, or (iii) unable to sustain level flight while flapping. Only 6 individuals (19%) gained altitude, 9 (29%) sustained level flight, and 16 (52%) consistently lost altitude. These performance groups differed in mean flight muscle ratio but not in wing loading (Table 2).

In contrast to these results for morphological determinants of flight performance, our surface-skimming experiments showed that performance increased steadily with increasing wing area, up to the highest relative wing areas observed (Fig. 3). Similarly, flight

Department of Biology, Pennsylvania State University, University Park, PA 16802, USA.

*To whom correspondence should be addressed.