Analytic treatment of cooperativity effects in supercooled liquids within the framework of the random-walk model

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(Received 21 March 1995)

An analytic treatment of cooperative effects in supercooled liquids within the framework of a random-walk model is presented. Cooperatively rearranging regions are shown to expand as the temperature T approaches a critical value T_k identified as the Kauzmann temperature. The model allows calculating susceptibility spectra and the T dependence of the average relaxation time. The results are in good agreement with existing experimental data.

PACS number(s): 64.70.Pf, 76.60.Es

Kinetic phenomena in supercooled liquids are known to be highly cooperative [1–3]. Interaction between randomly positioned particles creates a very complicated potential landscape for atoms and/or molecules that prevents a liquid from crystallization at the melting point T_m. Owing to the large number of metastable states with higher energies and sufficiently long lifetimes a system cannot attain the state with minimum energy. Another important consequence of strong interaction is the high degree of cooperativity of particle motion. One particle cannot change its position independently from its neighbors, implying that motion of a single particle should be considered together with corresponding changes in its surroundings. These microscopic features are responsible for a number of interesting and unusual properties of supercooled liquids [1,4] and render a first-principles theoretical description of the problem extremely difficult. The most elaborated current approach is the mode coupling theory (MCT) [3,5–7] which takes into account the interactions between real particles (atoms or molecules). It considers nonharmonic oscillations of a single particle, the effective friction force depending upon positions and velocities of the surrounding particles. Coupled nonharmonic oscillations lead to density fluctuations that govern the temperature dependence of the relaxation time in a self-consistent way, yielding the scaling law $\tau \propto (T-T_c)^{-\gamma}$ for the average relaxation time. The temperature T_c marks a dynamical singularity at which the density fluctuations vanish. Within the framework of the MCT this is equivalent to dynamic freezing of the system. It was recognized, however, that the divergence temperature T_c is not identical with the calorimetric glass transition temperature T_g at which the system becomes nonergodic. The MCT describes both the non-Arrhenius-type temperature dependence of average relaxation times for $T_m < T < T_c$ and the shape of susceptibility curves. It should be emphasized, however, that owing to the increasing degree of cooperativity computational difficulties of the MCT also increase with decreasing temperature and in its present form it fails to explain the behavior of supercooled liquids at temperatures close to T_g [3]. Currently there is no analytic theory that is able to explain experimental frequency-dependent susceptibility data within the temperature interval $T_g < T < T_c$ in which the MCT is not directly applicable.

Phenomenological approaches usually assume that a viscous liquid can be considered as an ensemble of so-called "cooperatively rearranging regions" or "structural units" [8–15]. They rest upon temperature dependences of different thermodynamic characteristics such as volume, entropy, or energy. The two former groups of models predict a Vogel-Fulcher-type temperature dependence of the average relaxation time τ [8,9],

$$\tau = \tau_0 \exp\left[\frac{A}{T-T_1}\right], \tag{1}$$

implying the divergence of the relaxation time at the temperature T_1. The entropy-controlled models associate this effect with a genuine second order phase transition to a state of zero configurational entropy, thus identifying T_1 with the Kauzmann temperature T_k [8]. In terms of statistical mechanics, the dynamical motion of the structural units and, concomitantly, the form of the temperature dependence of τ are connected with the topology of the potential energy landscape in configurational space [16,17].

In energy-controlled random-walk models (RWM's) structural units are considered to be atoms or molecules in particular surroundings. Their dynamics is described in terms of their random walk within a random potential landscape that reflects the local environment of a given particle [10–15]. These models are based on a master equation that governs the kinetics of jumps of structural units over potential barriers between metastable states [13,15]. At higher temperatures the time scale of fluctuations of the barrier heights separating local minima of the potential landscape is shorter than a characteristic jump time and structural units can execute jumps whenever barriers between metastable states happen to be sufficiently low. At lower temperatures a frozen-in distribution of barrier heights is established that determines the kinetics of structural units. This approach relates experimentally observed temperature dependences of relaxation times and frequencies to the energetic distribution of the density of possible metastable states (DPMS) of structural units determined by a large number of neighbors with random configurational coordinates [15]. Since

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quadratic spectral moments of these contributions do not necessarily exist, a stretched Gaussian function can be assumed as a both reasonable and sufficiently general ansatz for the DPMS distribution,

$$g(E)=g_0\exp\left[-\left[\frac{E}{kT_0}\right]^{\alpha}\right],\quad 1<\alpha<\infty\ , \tag{2}$$

where T_0 and α are the parameters of the DPMS distribution. For this distribution the RWM predicts a temperature dependence of the relaxation time of the form

$$\tau=\tau_0\exp\left[\alpha\left[\frac{T_0}{\alpha T}\right]^{\alpha/(\alpha-1)}\right]. \tag{3}$$

It has been shown before [15] that Eq. (3) provides a reasonably good fit for temperature dependences of relaxation times in many supercooled liquids within a temperature range extending from the melting point T_m to the glass transition temperature T_g. In addition, the RWM is able to predict—both analytically and by simulations—the occurrence of a kinetic freezing effect upon cooling and to recover the experimentally determined dependence of the glass transition temperature upon the cooling rate [14,15]. On the other hand, none of the existing phenomenological models is able to fit susceptibility spectra of supercooled melts. In particular, the RWM, though correctly reproducing temperature dependences of peak frequencies yields susceptibility spectra that are too broad.

Another common disadvantage of the above mentioned models is that they do not properly account for relatively long-range cooperative effects occurring in supercooled melts near T_g. In particular, the RWM in its original version does not consider interaction between different structural units whereas within the framework of the MCT this consideration is limited by highly complicated mathematical problems that until now can be solved neither analytically nor numerically. The present work is an attempt to incorporate cooperative effects into the framework of the RWM. By considering long-range cooperative effects the evolution of ordered regions within the disordered medium whose size increases with decreasing temperature is accounted for. At a certain critical temperature, identified as the Kauzmann temperature, the configurational entropy will be shown to vanish. Another consequence of the existence of cooperatively ordered regions is the narrowing of the distribution function for the energies of structural units and, concomitantly, of experimental susceptibility spectra. Evidence for the existence of long-range cooperative regions stems from light scattering experiments [18,19]. There are also indirect indications such as the sensitivity of T_g to the thickness of amorphous layers [20] and the increase of viscosity in thin layers [21].

In most disordered systems atoms or molecules interact via dipole moments. This is the case for networks of electric dipoles as well as electronic or nuclear spins. The following consideration is for electric dipoles; however, the generalization to other types of dipole-dipole interaction is straightforward. The potential energy u of two interacting dipoles is

$$u(\mathbf{r})=\frac{1}{4\pi\varepsilon\varepsilon_0}\left[\frac{(\mathbf{p}\cdot\mathbf{p}')}{r^3}-\frac{3(\mathbf{p}\cdot\mathbf{r})(\mathbf{p}'\cdot\mathbf{r})}{r^5}\right], \tag{4}$$

where r is their distance, $\mathbf{p}$ and $\mathbf{p}'$ are the dipole moments, ε_0 is the dielectric permittivity, and ε the dielectric constant. In disordered systems the spatial distribution of dipoles is characterized by both random distances and random orientations. Under these conditions the dipole contribution to the potential energy of a particle results from stochastic fluctuations [22]. However, dipole-dipole interaction within an ordered cluster will give an additional contribution to the potential energy. Consider a particle surrounded by other particles interacting according to a $u\propto 1/r^3$ law. Since the contribution dU from dipoles within a spherical layer extending from r to $r+dr$ to the total potential energy U of the particle is

$$dU\propto(1/r^3)(4\pi r^2dr)\propto(1/N)dN\ ,$$

N being the number of dipoles within the sphere of radius R, the dependence of U on the number of dipoles within an ordered cluster is $\propto\ln N$. As long as cooperativity increases upon cooling of a supercooled liquid one should consider this coupling energy when writing the master equation for the distribution function of the structural units.

Within the temperature range $T_g<T<T_c$ temporal fluctuations of the energy landscape in supercooled liquids are small and over-barrier jumps of structural units represent the dominating mode of structural rearrangements [15]. Since the structural unit encounters a new environment after having executing a jump "configurational memory" is likely to be lost after each jump, implying that the energies of successively visited metastable states are uncorrelated. Under these conditions a master equation for the normalized energy distribution function $f(E,t)$ of the structural units $[\int dE\, f(E,t)=1]$ can be formulated as

$$\frac{\partial}{\partial t}f(E,t)=\nu_0 g(E)\int_0^{\infty}dE' f(E',t)\exp\left\{-\frac{E'+E_k\ln[1+\Delta E f(E',t)]}{kT}\right\}$$
$$-\nu_0 f(E,t)\exp\left\{-\frac{E+E_k\ln[1+\Delta E f(E,t)]}{kT}\right\}, \tag{5}$$

where $g(E)$ is the normalized DPMS distribution function of structural units within a disordered environment $[\int dE\, g(E)=1]$, ν_0 an attempt-to-jump frequency, and k the Boltzmann constant. The first term on the right-hand side of Eq. (5) describes jumps into a given state from all other states and the second term corresponds to

jumps starting from the given state. The term $E_k \ln[1+\Delta E f(E,t)]$ describes the contribution to the activation energy of structural-unit jumps arising from the coupling among structural units. This term is written assuming that structural units with similar energies (within the energy domain $\sim\Delta E$) occupy configurationally similar metastable states with a concomitant increase in coupling energy within the ordered regions. The parameter E_k characterizes the strength of the dipole-dipole interaction [see Eq. (4)].

At temperatures above the glass transition temperature a supercooled melt is in quasi-equilibrium implying equilibrium distribution of structural units over metastable hopping states. This distribution is given by the equilibrium solution of Eq. (5),

$$f_{\rm eq}(E)=\left\{\int_0^\infty dE\left[g(E)\exp\left[\frac{E}{kT}\right]\right]^{1/[1-(E_K/kT)]}\right\}^{-1} \times\left[g(E)\exp\left[\frac{E}{kT}\right]\right]^{1/[1-(E_K/kT)]} . \quad (6)$$

Equation (6) represents an approximate solution of Eq. (5) for an energy interval near the maximum of the distribution function where $\Delta E f_{\rm eq}(E)>1$. Note that most structural units occupy states within this interval. Generally, a characteristic width of the distribution is determined by both the width of the DPMS function $g(E)$ and the temperature. The latter plays, nevertheless, a dominant role when the ratio E_k/kT approaches unity. In particular, at $T=E_K/k$ the function $f_{\rm eq}(E)$ approaches a δ function, $f_{\rm eq}(E)=\delta(E-E_m)$, with E_m being the energy at which the function $g(E)\exp(-E/E_k)$ reaches its maximum value. As long as there exists a correlation between positional and energetic characteristics of structural units this means that at $T=E_k/k$ all structural units have similar orientations and surroundings. Thus, Eq. (6) predicts zero configurational entropy of a supercooled liquid at a finite temperature. This state cannot, however, be realized experimentally since the coupling contribution to the activation energy of structural-unit jumps increases strongly as the distribution function becomes narrower with a concomitant increase of its peak value [see Eq. (5)]. Therefore an infinite time and/or an infinitesimal cooling rate are necessary to approach the state of zero configurational entropy. The above described effect is well known as the Kauzmann paradox [23]. E_K is thus directly related to the Kauzmann temperature, $E_K=kT_K$. On the other hand, the increase of the coupling energy with decreasing temperature indicates that both the number of particles that form an ordered region and the characteristic size of these regions also increase at lower temperatures.

The characteristic relaxation time is the inverse frequency of structural-unit jumps from the states corresponding to the maximum of the equilibrium distribution function. The DPMS given by Eq. (3) yields

$$\tau=\tau_0\left[1-\left[\frac{T_K}{T}\right]\right]^{-T_K/2T}\exp\left[\alpha\left[\frac{T_0}{\alpha T}\right]^{\alpha/(\alpha-1)}\right] . \quad (7)$$

For temperatures well above T_K Eq. (7) is practically identical with the temperature dependence of the relaxation time obtained from the RWM neglecting coupling of structural units. This reflects the high degree of disorder at higher temperatures that prevents structural units from coupling into ordered regions. For a sufficiently high cooling rate kinetic freezing of structural units may occur already within this temperature domain, implying a glass transition temperature well above the Kauzmann temperature. However, at sufficiently slow cooling rate the liquid may remain in equilibrium even at temperatures close to T_K. Then the first term in Eq. (7) becomes important. The divergence of this term at $T=T_K$ sets the lower temperature limit for the glass transition. Thus, within the context of the present model, the temperatures T_g and T_K are practically independent for high cooling rates but with decreasing cooling rate T_g approaches T_K. The temperature dependences of the characteristic relaxation time are presented in Fig. 1.

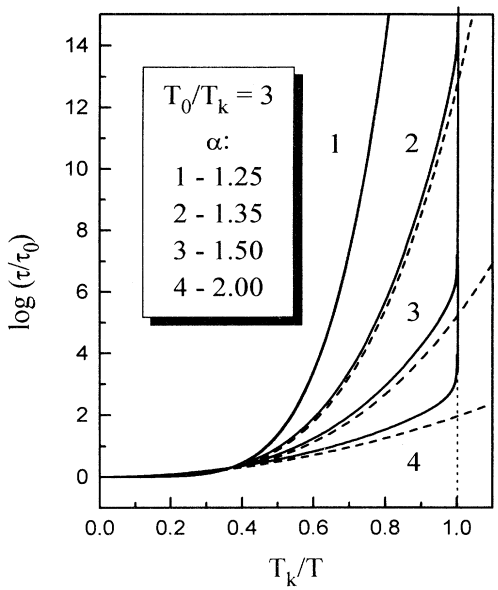

FIG. 1. Temperature dependences of the relaxation time. Solid curves are calculated from Eq. (7). Dashed lines are obtained from Eq. (3) neglecting coupling of structural units.

Knowledge of both the equilibrium distribution function for the energies of structural units and the dependence of the activation energy on the occupational density of states (DOS) allows calculation of susceptibility spectra for supercooled liquids according to

$$\chi(\nu)=\int_0^\infty dE\frac{(\nu/\nu_0)f_{\rm eq}(E)\exp(\{E+E_K\ln[1+\Delta E f_{\rm eq}(E)]\}/kT)}{1+(\nu/\nu_0)^2\exp(2\{E+E_K\ln[1+\Delta E f_{\rm eq}(E)]\}/kT)} . \quad (8)$$

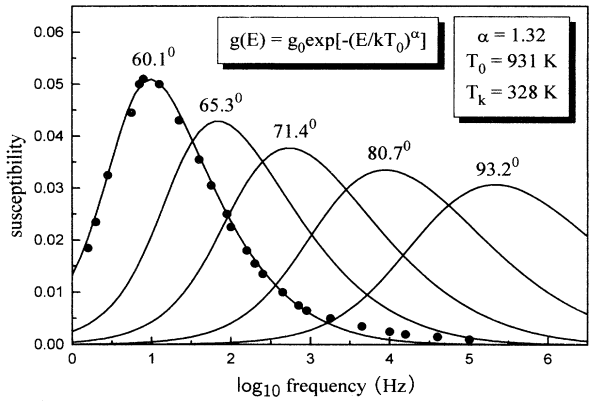

FIG. 2. Susceptibility spectra calculated from Eq. (8) for a stretched Gaussian DPMS. Experimental data for CKN are taken from [24].

Figure 2 shows a series of spectra obtained for a stretched Gaussian DOS. The spectra are asymmetric featuring a broader high frequency tail. Their widths exceed that of a Debye spectrum considerably. The T dependence of the peak maximum is in accord with the prediction of Eq. (7) for the parameter set chosen. Calculated $\chi(\nu)$ spectra are unspecific for the type of molecular motion involved while experimental spectra can be mode sensitive if only a subset of motions, such as dipole reorientations, contribute to an external signal. Nevertheless, experimental spectra for dielectric loss, mechanical stress relaxation, and heat capacity hardly differ from each other and are remarkably similar to spectra calculated via Eq. (8). As an example the dielectric loss spectrum for $0.4Ca(NO_3)_2$-$0.6KNO_3$ (CKN) recorded at 60 °C [24] are included in Fig. 2. These spectra have previously been fitted on the basis of a heuristically assumed stretched exponential relaxation function. The good agreement demonstrates that the present treatment provides a framework for interpreting susceptibility spectra on a more rigorous level.

On the other hand, most experimental susceptibility spectra become narrower with increasing temperature (see, e.g., [1]) while calculated spectra reveal the opposite trend. The latter effect is a consequence of the assumption of a rigid energy landscape. In reality temperature dependent vibrations lead to fluctuating heights of barriers separating metastable states. This will eventually lead to motional averaging effects and, ultimately, to the appearance of Debye-like spectra. Treatment of this effect within the framework of the RWM concept will be the subject of future work.

In summary, we have presented an analytic treatment of cooperative effects in supercooled liquids within the framework of a random-walk model describing the dynamics of structural units in energy space invoking dipole-dipole coupling. It predicts the existence of cooperatively rearranging regions that expand as T approaches a critical temperature T_K, identified as the Kauzmann temperature at which the configurational entropy vanishes. However, the completely ordered state is realized at infinitely slow cooling rates only. Otherwise a kinetic freezing effect intervenes that is responsible for the occurrence of (i) the calorimetric glass transition above T_K and (ii) the formation of ordered and disordered regions that persist at $T > T_g$. The proposed model predicts susceptibility spectra as well as the T dependence of the average relaxation frequency consistent with experimental data.

The authors are grateful to J. C. Dyre, E. W. Fischer, and R. Richert for helpful discussions. We thank H. Spindler for help with numerical calculations. This work has been supported by the Stiftung Volkswagenwerk.

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