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Ulrich Zürcher
Cleveland State University, u.zurcher@csuohio.edu

T. Keyes

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Configurational entropy and collective modes in normal and supercooled liquids

U. Zürcher* and T. Keyes†
Department of Chemistry, Boston University, Boston, Massachusetts 02215

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Soft vibrational modes have been used to explain anomalous thermal properties of glasses above 1 K. The soft-potential model consists of a collection of double-well potentials that are distorted by a linear term representing local stress in the liquid. Double-well modes contribute to the configurational entropy of the system. Based on the Adam-Gibbs theory of entropically driven relaxation in liquids, we show that the presence of stress drives the transition from Arrhenius to Zwanzig-Bässler temperature dependence of relaxation times. At some temperature below the glass transition, the energy scale is dominated by local stress, and soft modes are described by single wells only. It follows that the configurational entropy vanishes, in agreement with the ''Kauzmann paradox.'' We discuss a possible connection between soft vibrational modes and ultrafast processes that dominate liquid dynamics near the glass transition. [S1063-651X(99)12108-1]

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I. INTRODUCTION

The glass transition remains one of the challenges of chemical physics despite enormous advances in our understanding during the past two decades. The basic phenomenology of the transition is well established. As the temperature of a supercooled liquid is lowered even further, the specific heat (or heat capacity) drops rapidly without apparent changes in the structure (such as the nearest neighbor distribution) [1]. This decrease indicates the lack of kinetic accessibility of liquidlike degrees of freedom, and thus is a consequence of the transition between ergodic and nonergodic behavior [2].

The ergodic behavior in supercooled liquids and glasses has been studied in Ref. [3] using a molecular dynamics (MD) simulation. The authors define an energy metric which is zero for ergodic states and is nonzero when ergodicity is broken. They point out that this behavior is not surprising since symmetry breaking is already evident from the nonzero value of the zero-frequency shear modulus in glasses. Anderson outlined a theory in which elementary excitations are a consequence of the symmetry-broken state of the system [4]. Palmer proposed a two-level statistical scheme for treating broken ergodicity systems [5]. The number of such components is exponentially large ($\sim e^{\alpha N}$) [6].

Below 1 K the specific heat and the thermal conductivity have a linear and quadratic temperature dependence, respectively, i.e., $C(T)\sim T$ and $\kappa(T)\sim T^2$. Within the Debye model of crystal vibrations, the specific heat vanishes more rapidly as $T\rightarrow 0$, $C(T)\sim T^3$. Thus, the linear specific heat in glasses reflects additional degrees of freedom associated with disorder. Anderson, Halperin, and Varma [7] and Phillips [8] independently proposed that these states can be modeled by two-level systems (TLS) characterized by a continuous distribution of energy differences $n_{\rm TLS}(\Delta\epsilon/\epsilon^*_{\rm TLS})$, where $\epsilon^*_{\rm TLS}$ is some characteristic energy for TLS. The specific heat is then given by the variance of the energy differences,

$$C=\int_0^\infty n_{\rm TLS}(\Delta\epsilon/\epsilon^*_{\rm TLS})(\Delta\epsilon/T)^2 \times\exp(-\Delta\epsilon/T)/[1+\exp(-\Delta\epsilon/T)]^2\,d\Delta\epsilon.$$

Using $x=\Delta\epsilon/T$, we find

$$C=T\textstyle\int_0^\infty n_{\rm TLS}(xT/\epsilon^*_{\rm TLS})x^2e^{-x}/(1+e^{-x})^2dx.$$

For low temperatures, $T<\epsilon^*_{\rm TLS}$ and $n_{\rm TLS}(xT/\epsilon^*_{\rm TLS})$ is slowly varying. Assuming a flat distribution near the origin $\Delta\epsilon=0$, a linear temperature dependence follows, $C\sim n_{\rm TLS}(\Delta\epsilon\simeq 0)T$.

At higher temperatures, the thermal conductivity reaches a plateau and the specific heat rises faster than T^3 such that C/T^3 has a peak. Thermal properties of glasses over this extended temperature range have been described by the so called soft-potential model, which is an extension of the TLS model for glasses. Buchenau and co-workers have shown that two-level systems and low-energy vibrational states can be explained by the same distribution of localized modes [9]. Soft modes have been used to describe the excitation spectrum of glasses in the range $\nu\sim 10$ to 100 GHz that has anharmonic contributions from relaxation and quasiharmonic vibrational excitations (''boson peak'') [10]. It has been estimated that up to 100 particles participate in a low-frequency mode, $N_s\sim 10-100$. A detailed comparison of the predictions of the soft-potential model (SPM) with experiments has led to conflicting conclusions. While Sokolov and co-workers [11] found that the SPM does not explain the temperature dependence of the specific heat of $\mathrm{Ca_{0.4}K_{0.6}(NO_3)_{1.4}}$ near $T\simeq 1$ K, Lundqvist *et al.* found excellent agreement for other typical glass formers such as orthoterphenyl (OTP) and glycerol [12].

A typical glass temperature is about 100 K, while anomalous thermal properties of glasses are observed below 1 K. Near T_g, the heat capacity of supercooled liquids drops to crystallike values. This drop reflects the loss of configuration space accessible to the system in the glassy phase. As a

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*Author to whom correspondence should be addressed. Electronic address: zurcher@chem.bu.edu

†Electronic address: keyes@chem.bu.edu

consequence, the configurational entropy is much lower for a glass than for a liquid. Kauzmann observed that the *extrapolated* values of liquid entropies vanish at some temperature below the glass transition, $T_K < T_g$ [13].

This behavior suggests that thermally activated processes in the glassy phase are entropically driven [14]; the glass transition is regarded as an equilibrium second-order phase transition that is hidden by slow kinetics [15]. Gibbs and co-workers argued that particles in a liquid organize in *cooperatively rearranging regions* and determined the temperature dependence of the size of these regions. The relaxation time follows

$$\log \tau \sim \frac{1}{ST}, \tag{1}$$

where S is the specific entropy of the macroscopic sample and T is the temperature (in units with $k_B = 1$). In this paper, we use Eq. (1) to describe the temperature dependence of relaxation times.

The temperature dependence of $\log \tau$ is the basis of the classification of liquids into strong and fragile [16]. In a strong liquid, the relaxation time shows Arrhenius behavior, $\log \tau \propto 1/T$, all the way down to T_g [defined by $\tau(T_g) = 10^{13}\,\mathrm{P}$], while a fragile liquid exhibits a transition to stronger-than-Arrhenius dependence before T_g is reached. The drop in the specific heat $\Delta C = C(\text{liquid}) - C(\text{glass})$ correlates with the degree of fragility; ΔC is large for fragile liquids, while it is small, or even negligible, for strong liquids.

We show in this paper that super-Arrhenius behavior of relaxation times is consistent with a model of supercooled liquids in which localized, collective modes coexist with phonons. Similar to TLS modes for glasses below 1 K, such soft modes are intrinsic to the disordered state of the liquid. Thus, soft modes dominate the configurational entropy of liquids above the Kauzmann temperature, while the residual entropy below T_K originates mainly from TLS modes.

The soft-potential model is a collection of energy profiles along many-body coordinates, $V(x) = W[D_1 x - D_2 x^2 + x^4]$. The profiles are double and single wells for small and large values of the asymmetry, D_1, respectively. Buchenau argued that the asymmetry describes local (shear) stress in the liquid and proposed that its distribution is independent of temperature [17]. Since only double wells contribute to the configurational entropy, we expect local stress to govern much of low-temperature properties of liquids.

Well above the glass temperature, $T \gg T_g$, the system can surmount large barriers, local stress is only a small perturbation to the symmetric potential, $V(x) \simeq V_0(x) = W[-D_2 x^2 + x^4]$, and soft modes do not contribute to the specific heat. Since we have $C = T(\partial S/\partial T)$, the entropy does not depend on temperature and Eq. (1) gives Arrhenius behavior. The Adam-Gibbs theory is generally used to describe super-Arrhenius behavior, but our interest in the Arrhenius regime is to demonstrate the crossover from super-Arrhenius to Arrhenius temperature dependence only, for which the Adam-Gibbs ansatz should be applicable.

As the temperature is lowered, $T \gtrsim T_g$, the system surmounts small barriers only and the asymmetry between the minima of the wells can no longer be neglected. As a consequence, soft modes contribute to the specific heat. We introduce a distribution for asymmetry energies of soft modes, $n_{\mathrm{SPM}}(\Delta\epsilon/\epsilon^*_{\mathrm{SPM}})$, where $\epsilon^*_{\mathrm{SPM}}$ is the characteristic energy for soft modes. If $\epsilon^*_{\mathrm{SPM}}$ is much larger than the characteristic energy for TLS, $\epsilon^*_{\mathrm{SPM}} \gg \epsilon^*_{\mathrm{TLS}}$, then a system at temperature T can be in the high-temperature limit of the TLS model, $T/\epsilon^*_{\mathrm{TLS}} > 1$, and still remain in the low-temperature limit for soft modes, $T/\epsilon^*_{\mathrm{SPM}} < 1$.

For such temperatures, $T < \epsilon^*_{\mathrm{SPM}}$, we repeat our arguments from above to find that the configurational entropy vanishes linearly with temperature, $S(T) \sim n_{\mathrm{SPM}}(\Delta\epsilon \simeq 0) T$ [18]. Inserted into Eq. (1), we recover the Zwanzig-Bässler temperature dependence of relaxation times [19,20],

$$\log \tau \sim \frac{1}{n_{\mathrm{SPM}}(\Delta\epsilon \simeq 0) T^2}. \tag{2}$$

The linear temperature dependence of the configurational entropy for $T < T_g$ is unphysical, however, and should only be considered as an extrapolation. Indeed, this behavior has been derived assuming that $n_{\mathrm{SPM}}(\Delta\epsilon/\epsilon^*_{\mathrm{SPM}})$ is finite as $\Delta\epsilon \rightarrow 0$. For $T < T_g$, the energy scale is dominated by local stress so that the linear term in the soft-potential model is large, and soft modes are represented by single- and not by double-well potentials. It follows that the soft-mode contribution to the configurational entropy drops below the linear extrapolation, $S(T) < n_{\mathrm{SPM}}(\Delta\epsilon \simeq 0) T$, and then vanishes at some temperature below the glass temperature, $T_K < T_g$, in agreement with the ''Kauzmann paradox'' [13]. A schematic sketch of the temperature dependence of S is depicted in Fig. 1.

In an earlier paper, we calculated the density of states (DOS) of unstable frequencies within the soft-potential model [21]. We showed that the DOS depends on the frequency and temperature via the combination ν^2/T only, i.e., $\log G_u(\nu^2) \sim -\nu^2/T$ for $T \gg T_g$ and $\log G_u(\nu^2) \sim -\nu^4/T^2$ for $T \gtrsim T_g$. A frequency cutoff for double-well modes gives Arrhenius- and Zwanzig-Bässler dependence of the diffusion constant for high and low temperatures, respectively. However, in Ref. [21], no connection between unstable modes and thermodynamic quantities has been made.

Liquid dynamics may be formulated in terms of the motion of the system among the basins of the N-body potential energy via the ''reaction coordinates'' connecting them. We have suggested [22] that unstable modes are signatures of the reaction coordinates, and thus related to barrier crossing and diffusion. While that association must be made carefully, and the reaction coordinates are more complex than, e.g., simple parabolic barriers, the diffusion constant has been predicted very accurately from formulas based on the unstable modes. Here we additionally propose that unstable modes reflect the number of local minima accessible to the liquid in a neighborhood of a typical configuration. This is consistent with the association of unstable modes and reaction coordinates, since a configuration ''close'' to many basins most likely lies on several reaction coordinates.

If slow dynamics is governed by the configurational entropy from one point of view and by unstable modes from another, there should be a connection between the two. If the anomalous properties of liquids at low temperatures are due

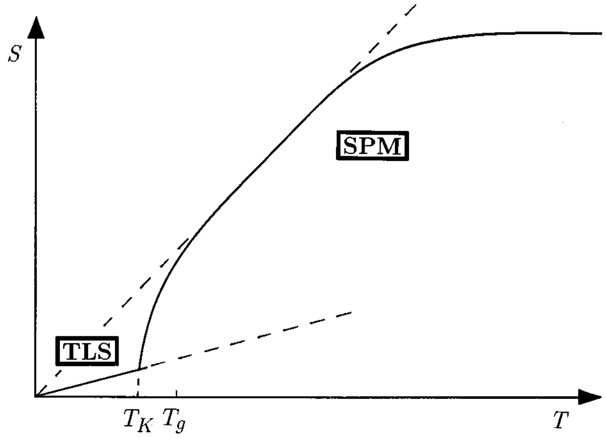

FIG. 1. Configurational entropy S vs temperature T (schematically). The extrapolation of S vanishes at the Kauzmann temperature T_K and T_g is the glass temperature. Also indicated are the linear behaviors discussed in the text.

to soft modes, then they also determine S. In the following we estimate a *frequency* and *temperature* dependent configurational entropy $S(\nu;T)$ from the contribution of soft modes with frequency ν. We then show that the unstable DOS $G_u(\nu)$, found in our prior calculations and in simulations, follows from a ν-dependent extension of Eq. (1) if $G_u(\nu)$ is identified as $\tau(\nu)$. Thus, the connection between the unstable modes and slow relaxation, and our prior calculation of the crossover from Arrhenius to Zwanzig-Bässler behavior, is greatly extended and clarified. In addition, the soft-potential model gives a complete description of the characteristic behavior of the configurational entropy in glass-forming liquids, cf. Fig. 1, in which the temperature dependence is governed by local stress.

II. SOFT VIBRATIONAL MODES IN LIQUIDS

Since the configurational entropy reflects the topology of the potential energy surface, S can be computed in the limit $T\rightarrow\infty$. In particular, we use a definition of S that is closely related to the density of local minima. This density plays an important role in the ‘‘energy landscape’’ picture of glass formation [16]. For an arbitrary liquid configuration $\vec{R}_0$, we find the nearest local minimum of the potential energy surface, $\vec{R}_{\rm min}$, by displacing the coordinates of the particles participating in a low-frequency vibrational mode [6]. We expand the potential energy around $\vec{R}_0$, $\Delta\Phi=\Phi(\vec{R})-\Phi(\vec{R}_0)\simeq-\vec{F}\cdot(\vec{R}-\vec{R}_0)+\frac{1}{2}(\vec{R}-\vec{R}_0)\cdot\mathbf{K}\cdot(\vec{R}-\vec{R}_0)$. Since N_s does not scale with the total number of particles, the potential difference is given by $\langle\Delta\Phi\rangle\sim W$, where W is an energy scale for particle interactions. Hence, the average distance to the nearest minimum $\Delta R=\langle|\vec{R}_0-\vec{R}_{\rm min}|\rangle$ follows $(\Delta R)^2\sim W/\Omega^2$, where Ω is an upper frequency cutoff for soft vibrational modes, $\langle\mathbf{K}\rangle\sim\Omega^2\mathbf{I}$. We denote by Δx_0 the separation of the minima of two-level systems. Because the configurational entropy is the statistical quantity related to the number of *microscopic* states corresponding to the same *macroscopic* state, we have in harmonic approximation $S\sim(\Delta R/\Delta x_0)^2$. We show below that the entropy is well defined in the limit $W\rightarrow 0$.

At temperatures well above the glass transition, we expect that relaxation times obey Arrhenius behavior, $\log\tau\sim$const/T, or $S(T)=$const, for $T\gg T_g$. It follows that the specific heat vanishes, $C=0$, and hence soft modes are described by *symmetric* double wells,

$$V_0(x)=W[-D_2x^2+x^4]. \tag{3}$$

Here, the parameter D_2 is a random variable for which we assume a uniform distribution,

$$p_2(D_2)=\text{const},\quad \text{for } 0<D_2<\frac{\Omega^2}{4W}. \tag{4}$$

The potential is symmetric $V_0(x)=V_0(-x)$, with two minima located at $x_0^{\pm}=\pm\sqrt{D_2/2}$. The minima are separated by the potential barrier $\Delta V_0=WD_2^2/4$. The barrier curvature is the negative second derivative of the potential, $\nu^2=-d^2V_0/dx^2=W[2D_2-12x^2]$. Since $x\simeq 0$ near the top of the barrier, barrier frequencies characterize soft modes, $\nu^2\simeq 2WD_2$. The separation of potential minima, $\Delta x_0=x_0^+-x_0^-$, thus follows $\Delta x_0=\nu/\sqrt{W}$. We thus find that the configurational entropy depends on the barrier frequency of the soft mode,

$$S(\nu)\sim\frac{W^2}{\Omega^2\nu^2},\quad T\gg T_g. \tag{5}$$

At low temperatures, the supercooled liquid supports long-range stress fields [23]. Long-range stress fields induce *frustration* so that the supercooled liquid is the high-entropy phase of the system [24]. In this phase, the energy landscape has high density of local mimina. The characteristic energy scale of collective modes is now proportional to the displacement, $\delta\Phi\simeq WD_1\Delta R'$. Setting $\delta\Phi\simeq W$, the typical deviation follows $(\Delta R')^2\sim 1/\langle D_1^2\rangle$. In the presence of stress, the majority of two-level systems are asymmetric double wells. Because the number of particles participating in a soft mode does not change in the presence of stress, the potential difference $\Delta\Phi'\sim\Omega^2(\Delta R')^2$ gives an estimate of the ratio of the number of asymmetric TLS to the number of symmetric TLS, $\kappa\sim\langle\Delta\Phi'\rangle/W\sim\Omega^2/W\langle D_1^2\rangle$.

Thus, for $T\gtrsim T_g$, soft vibrational modes are represented by both double- and single-well potentials,

$$V(x)=W[D_1x-D_2x^2+x^4]. \tag{6}$$

Here, the parameter D_1 is a random variable characterized by the probability distribution $p_1(D_1)$. Because two soft modes that differ only in the sign of D_1 are equivalent, the distribution is symmetric, $p_1(D_1)=p_1(-D_1)$. Assuming Gaussian statistics for D_1, the distribution is characterized by the second moment, $p_1(D_1)=\sqrt{2/\pi}\langle D_1^2\rangle^{1/2}\exp(-D_1^2/\langle D_1^2\rangle)$. In the limit $T_g\rightarrow 0$, the variance vanishes $\langle D_1^2\rangle\rightarrow 0$, and soft modes are represented by symmetric double wells only, $p_1(D_1)=\delta(D_1)$.

Since the parameter D_1 describes thermal stress in the liquid, $\langle D_1^2\rangle$ follows from thermodynamic considerations. At temperature T, soft modes with $\Delta V_0<T$ are in either state with equal probability and thus contribute to the entropy, while contributions from modes with $\Delta V_0>T$ are much reduced. Kauzmann argued that the entropy of a glass vanishes below some temperature T_K [13]. In the two-level description of supercooled liquids, a thermodynamic state with zero entropy is represented by a collection of soft modes, all of which are single wells. It follows that the asymmetry is large for modes with $\Delta V_0 < T_K$. In linear order in D_1, the asymmetry is given by $\Delta\epsilon \simeq W D_1 \Delta x_0 = \sqrt{2} W D_1 D_2^{1/2}$. The asymmetry is large for $\Delta\epsilon \sim \Delta V_0$, or

$$D_1 \sim D_2^{3/2} \quad \text{(single/double wells)}. \tag{7}$$

From $\Delta V_0 \sim T_K$, we have $D_2 \sim (T_K/W)^{1/2}$ and thus arrive at the estimate $\langle D_1^2 \rangle \sim (T_K/W)^{3/2}$. Buchenau identified the glass transition temperature T_g with Kauzmann temperature T_K, and arrived at an explicit expression for $p_1(D_1)$ using a different approach [17]. Here, we do not use this identification and have

$$p_1(D_1) = 0.231\left(\frac{T_K}{W}\right)^{3/4} \exp\left[-0.169\left(\frac{W}{T_K}\right)^{3/2} D_1^2\right]. \tag{8}$$

This distribution guarantees that the specific entropy is exponentially small for temperatures $T < T_K$, in agreement with the ''Kauzmann paradox.''

For $T > T_K$, the supercooled liquid probes soft modes represented by both single- and double-well potentials. Since $D_2 \simeq \nu^2/2W$, Eq. (7) gives an upper bound for D_1 that depends on the barrier frequency, $D_1 < \nu^3/16W^{3/2}$. Consequently, the asymmetry as well has an upper bound that depends on ν, $\Delta\epsilon < \Delta\epsilon_{\max} \sim \nu^4/W$. Following Ref. [7], the level density is assumed to be flat, i.e., $n_{\mathrm{SPM}}(\Delta\epsilon) \simeq n_{\mathrm{SPM}}(\Delta\epsilon \simeq 0)$ for $\Delta\epsilon < \Delta\epsilon_{\max}$ and $n_{\mathrm{SPM}}(\Delta\epsilon) \simeq 0$ for $\Delta\epsilon > \Delta\epsilon_{\max}$. The ratio of the number of asymmetric TLS to the number of symmetric TLS can be written $\kappa \sim n_{\mathrm{SPM}}(\Delta\epsilon \simeq 0)\Delta\epsilon_{\max}$. We readily find the level density $n_{\mathrm{SPM}}(\Delta\epsilon \simeq 0) \sim W^{3/2}\Omega^2/T_K^{3/2}\nu^4$. Since $S \sim n_{\mathrm{SPM}}(\Delta\epsilon \simeq 0)T$, we now have, for the specific entropy,

$$S(\nu;T) \sim \frac{W^{3/2}\Omega^2}{T_K^{3/2}\nu^4} T, \quad T \gtrsim T_g. \tag{9}$$

In Ref. [21], we used the soft-potential model to calculate the density of barrier frequencies, $G_u(\nu^2;T) = \langle \delta(d^2V/dx^2 + \nu^2) \rangle$, where the average is taken with respect to the coordinate, x, and the parameters of the soft potential, D_1 and D_2. The temperature dependence arises by assuming the thermal equilibrium distribution for local coordinates, $p(x) \sim \exp[-V(x)/T]$. We introduced scaled frequencies and temperatures, $\nu' = \nu/\sqrt{W}$, $\Omega' = \Omega/\sqrt{W}$, and $T' = T/W$, and then derived exact expressions for the density in the limit $W \to 0$. We found that the onset of stress in the liquid governs the frequency and temperature dependence of the density. For high temperatures, $T \gg T_K$, we found that thermal stress is negligible and the density obeys Arrhenius temperature dependence, $\log G_u(\nu^2;T) \sim -\Omega^2\nu^2/T$. For low temperatures, $T \gtrsim T_K$, on the other hand, thermal stress is large and density follows Zwanzig-Bässler temperature dependence, $\log G_u(\nu^2;T) \sim -T_K^{3/2}\nu^4/\Omega^2 T$. A comparison with Eqs. (5) and (9) shows that $G_u(\nu^2;T)$ depends on the frequency-dependent configurational entropy via an extension of the Adam-Gibbs relation, $G_u(\nu^2;T) \sim \exp[-1/S(\nu;T)T]$. This role of stress in liquids is supported by findings from a molecular dynamics study of a model glass [23]. The authors found that stress fields are disrupted by thermal excitations in normal liquids above some temperature T_s $(T_s > T_g)$. As the temperature is lowered, the local structure becomes more correlated so that long-range stress fields can be supported by the disordered state of supercooled liquids below T_s. The authors propose that the *percolation* of such correlated regions then leads to the glass transition.

Equation (7) defines a frequency cutoff for double-well potentials, $\nu_c \sim T_K^{1/4}$. For $\nu > \nu_c$ soft modes are double-well potentials, while single wells dominate for $\nu < \nu_c$. Since single wells do not contribute to the configurational entropy, the structural relaxation time follows $\tau^{-1} \sim \int_{\nu_c}^{\infty} \exp[-1/S(\nu;T)T]d\nu$, or in leading order,

$$\log \tau \sim \frac{1}{S(\nu_c;T)T}. \tag{10}$$

From Eqs. (5) and (9) we thus find that the appearance of long-range stress fields in the liquid drives the crossover from Arrhenius behavior for temperatures well above the transition, $T \gg T_g$, to Zwanzig-Bässler behavior in the vicinity of the glass temperature, $T \gtrsim T_g$. We emphasize that we have not derived this result from first principles, however, since we have used this temperature dependence to identify the parts of the soft-potential model and derive their distributions.

Elementary excitations are a consequence of the symmetry-broken state of the system [4] and can be identified by diagonalizing the force matrix $\mathbf{K}$ of the many-body system. For a liquid, a unique reference configuration does not exist, and the average over many configuration is taken to find the (normalized) spectrum of the liquid state. Liquid dynamics is solidlike for times much shorter than the ''Maxwell time'' [25,26]. Instantaneous normal modes (INM) have been used in recent years to describe liquid dynamics on picosecond time scales [27,28]. The success of theories based on dynamic properties on (ultra-) short time scales is a consequence of the elastic resistance to shear stress for short times, which itself stems from the nonzero value of the zero-frequency shear modulus.

The INM spectrum extends to both real and imaginary frequencies. The high-frequency tail of the real lobe originates from two-particle collisions. The frequency and temperature dependence of the unstable lobe is consistent with Eqs. (5) and (9) for high and low temperatures, respectively, with a crossover above the melting temperature [29]. Furthermore, the contribution of double-well modes to the unstable lobe vanishes at some finite imaginary frequency, $\nu_c^2 < 0$. While the unstable lobe of the INM density contains ''false barrier'' modes [30], the barrier density in the soft-potential model does not. Thus, the striking similarity of the two densities suggests that instantaneous normal modes are effective in probing ''channels'' for diffusion.

Since soft vibrational modes describe the mesoscopic dynamics that is exhibited, e.g., in the boson peak [10], Eq. (10) suggests a connection between structural relaxation and vibrational properties of glass-forming liquids on (ultra-) short time scales. In Ref. [21], we identified oscillations around the potential minima of soft modes with fast β processes in liquids. Equation (10) then gives the relation [31]

$$\log \tau \sim \frac{1}{\langle x^2 \rangle_\beta}, \tag{11}$$

which is the basis of much of the work on glass transition on short time scales, particularly in proteins [16]. In proteins, the minima of soft modes correspond to *conformational substates*, which were first used to interpret the nonexponential time dependence of the CO rebinding on myoglobin after photodissociation [32].

Excellent candidates for exploring soft modes and the role of fast processes in glassy dynamics are ''bottleneck'' and saturation experiments and nonlinear phenomena associated with two-level systems [1]. In fact, pure dephasing has recently been measured in picosecond vibrational echo experiments of myoglobin CO [33]. It shows a power-law behavior and then becomes thermally activated, $1/T_2^* = aT^\alpha + b\exp(-\Delta E/T)$. A detailed study of such temperature dependence will greatly enhance our understanding of relaxation and the nature of low-frequency vibrational excitations in glasses.

III. DISCUSSION

Near the glass transition, the heat capacity of a supercooled liquid drops to crystallike values. This observation connects the dramatic increase of relaxation times near T_g to an underlying equilibrium second-order phase transition. Adam and Gibbs proposed that thermally activated processes are entropically driven, $\log \tau \propto 1/ST$, where S is the configurational entropy of the liquid. The fraction of configuration space accessible to the system, and thus the configurational entropy, decreases as the temperature is lowered.

The configurational entropy reflects the disordered structure of the liquid. It is solidlike at short distances only, while translational invariance is destroyed at long distances. As a consequence, the vibrational spectrum is dominated by phonons and soft modes at high and low frequencies, respectively. Collective modes are characterized by potential energies along their many-body coordinates, and the softening of vibrational modes is described by symmetric double wells. The presence of long-range stress in the liquid enters this description via the asymmetry between the local minima of double-well modes, i.e., the linear term in the soft-potential model.

We have shown that local stress governs the temperature dependence of the configurational entropy. At high temperatures, $T \gg T_g$, local stress is negligibly small and a distribution of symmetric double-well modes gives a temperature independent entropy, $S(\nu) \sim W^2/\Omega^2\nu^2$. Local stress becomes large as the temperature is lowered, $T \gtrsim T_g$. A distribution of asymmetric double-well modes then gives an entropy that is linear in temperature, $S(\nu;T) \sim (W^{3/2}\Omega^2/T_K^{3/2}\nu^4)T$. The linear term in the soft-potential model introduces a frequency cutoff for double-well modes, $\nu_c \sim T_K^{1/4}$. At temperatures below the glass transition, local stress dominates the energy scale and soft modes are described by single-well potentials. As a consequence, the configurational entropy vanishes at the Kauzmann temperature, $S(\nu;T=T_K)=0$. Generalizing the Adam-Gibbs ansatz, we have for the relaxation time $\log \tau \sim 1/S(\nu_c;T)$, and find Arrhenius and Zwanzig-Bässler temperature behavior of relaxation times at high and low temperatures, respectively.

We note that the vibrational spectrum reflects solidlike properties of supercooled liquids, while the Adam-Gibbs expression emphasizes liquidlike aspects of the glass transition [16]. We are not first trying to relate liquid- and solidlike properties of glass-forming liquids. Indeed, the relation between relaxation times in liquids and the mean-square displacements on picosecond time scales, cf. Eq. (11), had previously been proposed without reference to the liquid state [34]. From the heuristic arguments presented in this paper, we speculate that liquidlike and solidlike ''views'' of the glass transition are not in conflict with each other, but are rather related on a fundamental level.

In future papers, we plan to explore in greater detail the ideas outlined here. Of particular interest is the nature and characterization of soft modes and how they are related to TLS. Furthermore, our approach to the glass transition bears some resemblance to the solidlike treatment of supercooled liquids and glasses in a recent report by Alexander [35]. The role of stresses is different in the two approaches, however, and the underlying physical assumptions must be carefully reexamined.

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[1] P. W. Anderson, in *Ill Condensed Matter*, edited by R. Balian, R. Maynard, and G. Toulouse (North-Holland, Amsterdam, 1979).

[2] R. G. Palmer and D. L. Stein, in *Relaxations in Complex Systems*, edited by K. Ngai and G. B. Wright (National Technical Information Service, U.S. Department of Commerce, Springfield, VA, 1984).

[3] D. Thirumalai, R. D. Mountain, and T. R. Kirkpatrick, Phys. Rev. A **39**, 3563 (1989).

[4] P. W. Anderson, *Basic Notions of Condensed Matter Physics* (Benjamin, Menlo Park, CA, 1984).

[5] R. G. Palmer, Adv. Phys. **31**, 669 (1982).

[6] F. H. Stillinger and T. A. Weber, Science **225**, 983 (1984).

[7] P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).

[8] W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).

[9] U. Buchenau, H. M. Zhou, N. Nücker, K. S. Gilroy, and W. A. Phillips, Phys. Rev. Lett. **60**, 1318 (1988).

[10] A. P. Sokolov, Science **273**, 1675 (1996).

[11] A. P. Sokolov, R. Calemczuk, B. Salce, A. Kisliuk, D. Quitmann, and E. Duval, Phys. Rev. Lett. **78**, 2405 (1997).

[12] A. Lundqvist, O. Yamamuro, I. Tsukushi, and T. Matsuo, J. Chem. Phys. **107**, 5103 (1997).

[13] W. Kauzmann, Chem. Rev. **43**, 219 (1948).

[14] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).

[15] J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys. **28**, 373 (1958).

[16] C. A. Angell, Science **267**, 1924 (1995).

[17] U. Buchenau, Philos. Mag. B **65**, 303 (1992).

[18] Integration gives $S(T)-S(0)\sim n_{\mathrm{SPM}}(\Delta\epsilon\simeq 0)T$. Because the entropy vanishes at $T=0$, we have $S(0)=0$ and thus find $S(T)$ given in the text.

[19] R. Zwanzig, Proc. Natl. Acad. Sci. USA **85**, 2029 (1988).

[20] H. Bässler, Phys. Rev. Lett. **58**, 767 (1987).

[21] U. Zürcher and T. Keyes, Phys. Rev. E **55**, 6917 (1997).

[22] T. Keyes, J. Chem. Phys. **101**, 5081 (1994).

[23] S.-P. Chen, T. Egami, and V. Vitek, Phys. Rev. B **37**, 2440 (1988).

[24] C. A. Angell, Proc. Natl. Acad. Sci. USA **92**, 6675 (1995).

[25] J. C. Maxwell, Philos. Mag. **157**, 49 (1867).

[26] J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955).

[27] T. Keyes, J. Phys. Chem. **101**, 2921 (1997).

[28] R. M. Stratt, Acc. Chem. Phys. **28**, 201 (1995).

[29] U. Zürcher and T. Keyes, in *Supercooled Liquids: Advances and Novel Applications*, edited by J. F. Fourkas, *et al.* (American Chemical Society, Washington, DC, 1997).

[30] J. Gezelter, E. Rabani, and B. J. Berne, J. Chem. Phys. **107**, 4618 (1997).

[31] U. Buchenau and R. Zorn, Europhys. Lett. **18**, 523 (1992).

[32] H. Frauenfelder, S. G. Sligar, and P. G. Wolynes, Science **254**, 1598 (1991).

[33] C. W. Rella, K. D. Rector, A. Kwok, J. R. Hill, H. A. Schwettman, D. D. Dlott, and M. D. Fayer, J. Phys. Chem. **100**, 15 620 (1996).

[34] R. Hall and P. G. Wolynes, J. Chem. Phys. **86**, 2943 (1987).

[35] S. Alexander, Phys. Rep. **296**, 65 (1998).