

Mesoscopic Mean-Field Theory for Supercooled Liquids and the Glass Transition

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The Weiss mean-field theory is applied to finite systems with unrestricted sizes, yielding a partition function for supercooled liquids. Finite-size effects broaden the transition and induce a Curie-Weiss-like energy reduction which provides an explanation for the Vogel-Tamman-Fulcher law. Because the energy reduction is intensive, the basic thermodynamic unit (aggregate) subdivides into smaller regions (clusters) which lowers the net internal energy. The distribution of aggregate sizes, combined with a relaxation rate that varies exponentially with inverse size, provides an explanation for the Kohlrausch-Williams-Watts law. [S0031-9007(99)08725-6]

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Any liquid that is supercooled sufficiently below its normal freezing point will exhibit abrupt changes in its thermal and dynamic properties near a glass temperature T_g [1]. Such supercooled liquids are often classified by their distinctive time t - and temperature T -dependent behavior. Relaxation measurements are usually analyzed in terms of the Kohlrausch-Williams-Watts (KWW) stretched exponential $\Phi(t) \propto e^{-(t/\tau)^\beta}$, with the Vogel-Tamman-Fulcher (VTF) law for the characteristic relaxation time $\tau \propto e^{B/(T-T_0)}$. Here β is the KWW stretching exponent, T_0 is the Vogel temperature, and kB gives an energy scale for activation. The most commonly observed nonexponential response has $\beta < 1$, and non-Arrhenius activation behavior has $T_0 > 0$, but there is still no widely accepted explanation for either formula. Here we extend standard mean-field theory to mesoscopic systems and obtain a partition function for supercooled liquids. Our approach is an empirically motivated adaptation of the theory of finite-size thermostatics developed by Hill [2]. The main new feature is a connection between the Curie-Weiss law from magnetism and the VTF-like behavior [3,4] of supercooled liquids. When combined with a model for size-dependent relaxation rates [5], the theory also gives good agreement with measured KWW-like response [6,7] and a quantitative correlation to measured heat capacities [8,9]. Thus, the behavior near T_g can be attributed to a thermal transition within mesoscopic domains.

Most experimental evidence now favors the domain picture for the primary response of supercooled liquids [10]. One of the techniques is nonresonant spectral hole burning (NSHB) [11], where different low-frequency electric fields are absorbed by distinct slow degrees of freedom. NSHB works because the slow degrees of freedom are sufficiently independent from the thermal bath that most of the energy they absorb remains localized during their response. Local-probe measurements [12,13] on polyvinylacetate (PVAc) have determined that near T_g the radius of dynamic correlation is 2–7 nm.

Consider a cluster containing a total of m degrees of freedom. In the Ising model, the i th degree of freedom

may be represented by a “particle” with a state variable (σ_i) that is either “up” (+1) or “down” (−1). Assuming a uniform interaction energy (ε_0/γ) between each particle and its γ nearest neighbors, the net internal energy per particle is the sum over all pairs of interacting particles, $\varepsilon_m = -(\varepsilon_0/\gamma m) \sum \sigma_i \sigma_j$. For magnetic systems, σ_i represents the orientation of an Ising spin. For supercooled liquids, σ_i could correspond to a quasistatic position or dynamic phase of a molecule. Although it may be unrealistic to assume only binary degrees of freedom for real molecules in glass-forming liquids, the simplified model presented here seems adequate as a first step toward describing several salient features. Thus, for simplicity, we assume that each molecule with multiple degrees of freedom may be represented by multiple Ising-like particles.

In general, ε_m will depend on the relative “alignment” (position or phase) of each particle and its neighbors. If the cluster is large enough and the interaction long ranged enough, a mean-field approximation may be used to replace the actual state of all neighbors by the net alignment of the entire cluster. Assuming a total of ℓ up particles and $m - \ell$ down particles, with the Bragg-Williams mean-field formalism, the interaction energy per particle may be written $\varepsilon_m(\ell) = -\frac{1}{2}\varepsilon_0(2\ell/m - 1)^2$. Using the binomial coefficient for the degeneracy of each configuration, the partition function of the cluster is

$$\Delta_m = \sum_{\ell=0}^m \frac{m!}{(m-\ell)!\ell!} e^{-m\varepsilon_m(\ell)/kT}. \quad (1)$$

For analytic evaluation it is convenient to make a change of variables to $L = 2\ell/m - 1$, leaving $\varepsilon(L) = -\frac{1}{2}\varepsilon_0 L^2$. Note that the magnitude ($|L|$) is a type of order parameter, and that the energy is a maximum when there is no order, $\varepsilon(0) = 0$, and it is a minimum when the cluster is fully aligned, $\varepsilon(\pm 1) = -\varepsilon_0/2$. For large m , using Stirling’s approximation for the factorials and converting the sum to an integral, the partition function becomes $\Delta_m \approx \int_{-1}^{+1} dL e^{-m\varepsilon(L)/kT}$, where the free energy per particle is $f(L) \approx \varepsilon(L) + \frac{1}{2}kT\{(1+L)\ln[\frac{1}{2}(1+L)] + (1-L)\ln[\frac{1}{2}(1-L)]\}$. If $m \rightarrow \infty$, only the minimum free energy contributes to the partition function, and

setting $\partial f(L)/\partial L = 0$ yields the usual transcendental equation for the order parameter, $L_\infty = \tanh[L_\infty(\varepsilon_0/kT)]$. This solution exhibits the well-known Curie-Weiss transition at $T = \varepsilon_0/k$, with $L_\infty = 0$ and hence $\varepsilon(L_\infty) = 0$ for $T > \varepsilon_0/k$, but this standard result is valid only in the macroscopic limit. We now show that a mesoscopic system can lower its energy by subdividing into smaller clusters.

Continuing with the integral representation, the average energy for a cluster of size m is $E_m \approx \int_{-1}^1 dL (-\frac{1}{2}\varepsilon_0 L^2) e^{-mf(L)/kT} / \Delta_m$. For large but finite m , the integrals may be approximated by a steepest-descents procedure. Specifically, for the denominator at $T > \varepsilon_0/k$ where $L_\infty = 0$, $\Delta_m \approx 2^m \sqrt{2\pi/m(1 - \varepsilon_0/kT)}$. However the extra factor of L^2 in the numerator yields a different transcendental equation $L_m \approx \tanh[L_m(\varepsilon_0/kT) + 2/(mL_m)]$, which leads to a nonzero order parameter $L_m \approx \sqrt{2/m(1 - \varepsilon_0/kT)}$ and a nonzero energy reduction $E_m \approx -\frac{1}{2}\varepsilon_0/(1 - \varepsilon_0/kT)$ above the transition. Note that $L_m \propto m^{-1/2}$ and the total energy is intensive, effectively independent of size, thereby returning the standard mean-field result that an infinite cluster at $T > \varepsilon_0/k$ is unordered, with negligible energy density. Our main conclusion is that, when applied to finite clusters, the same mean-field theory yields Curie-Weiss-like energies which can be used to explain the VTF law in supercooled liquids. A specific model is as follows.

Returning to the explicit summation of Eq. (1), we now consider clusters that are in contact with a bath of particles at chemical potential μ . This induces a range of cluster sizes $m_0 \leq m < \infty$, where m_0 is a minimum cluster size, which may be related to the minimum number of particles necessary for the mean-field approximation of Δ_m . The partition function becomes

$$\Gamma = \sum_{m=m_0}^{\infty} \Delta_m e^{m\mu/kT}. \quad (2)$$

Presumably m_0 requires a central particle and at least one shell of nearest neighbors, which for random close-packed spheres would involve about 13 particles. Particles with steric constraints might have somewhat less than ideal close packing, and indeed all but one of the substances we have analyzed have $m_0 = 8-12$ (Table I). Salol has the unusual value of $m_0 = 24$, possibly due to the O-H bond between molecules. Although Eq. (2) resembles the grand-canonical ensemble, in fact, Γ contains only the intensive variables μ and T (pressure can be ignored for liquids which are effectively incompressible), so that the cluster volumes are not fixed. If the summation included all cluster sizes $1 \leq m < \infty$, then Γ would be in the ‘‘generalized’’ ensemble [2]. This completely open ensemble is rarely used for macroscopic systems, where the three intensive variables cannot be independent, but it is the only ensemble that does not externally restrict the sizes of mesoscopic systems. The small clusters missing from Eq. (2) are compensated for by including an average fraction (f) of free particles between the clusters in Eq. (3) below.

TABLE I. Glass temperature (T_g) and transition midpoint (T_m , where $|\bar{L}| = \frac{1}{2}$) for methyltetrahydrofuran (MT), propylene carbonate (PC), salol (SA), PVAc, propylene glycol (PG), and glycerol (GL). Best fits to the peak dielectric loss as a function of temperature [3,4] yield the net interaction energy (ε_0/k), fraction of free particles (f), frequency prefactor (ν_0), and minimum cluster size (m_0).

	T_g (K)	T_m (K)	ε_0/k (K)	f	ν_0 (THz)	m_0
MT	91.5	89.3	100	0.086	0.031	9
PCAc	163	160	182	0.086	0.021	12
SA	217	225	257	0.079	0.014	24
PV	299	240	272	0.050	0.046	9
PG	167	92.5	105	≈ 0	7.7	8
GL	188	107	121	≈ 0	28	9

Finally we assume that n clusters group together to form an aggregate, and that the clusters are in dynamic equilibrium with the free particles in the aggregate so that the clusters are indistinguishable. The partition function becomes

$$Y = \sum_{n=1}^{\infty} \frac{\Gamma^n}{n!} e^{nf\bar{m}\mu/kT}, \quad (3)$$

where $\bar{m} = kT \partial \ln \Gamma / \partial \mu$ is the average number of particles in a cluster. Note that f is an effectively constant geometric ratio, and that the filling factor of the clusters is $1/(1+f)$. For random close-packed uniform hard spheres, $f = 0.57$, whereas for realistic clusters which vary in size and need not be spherical, $f \ll 0.57$ (Table I). Typical values of f are similar to the fraction of mobile molecules found in a molecular-dynamics simulation, 0.055 ± 0.005 [14], but we emphasize that in our picture the primary response is due to the activated relaxation of all particles in each aggregate.

Thermal equilibrium is found from Gibbs’ variational principle by adjusting μ to maximize Y with all other variables fixed, $(\partial Y / \partial \mu)_{f, \varepsilon_0, T} = 0$. Thus, the thermal behavior of a given substance is governed by only two basic parameters: f controls both the average number of particles in a cluster (\bar{m}) and average number of clusters in an aggregate ($\bar{n} = \Gamma \partial \ln Y / \partial \Gamma$), while ε_0/k simply shifts the temperature of the transition. [Glycerol and PG differ in that they have a vanishingly small f , possibly due to the hydrogen bonding between molecules. For these ‘‘strong’’ liquids we set $f = 0$ in Eq. (3) and adjust μ/kT in Eq. (2) to the constant value which best fits the data.] Recall that the energy of an average cluster exhibits Curie-Weiss-like behavior so that the energy of an average aggregate may be written $\bar{E} \approx \bar{n} E_m \approx \bar{n} [-\frac{1}{2}\varepsilon_0/(1 - \varepsilon_0/kT)]$. Using this activation energy in the Arrhenius law ($e^{-\bar{E}/kT}$) yields VTF-like behavior with $T_0 = \varepsilon_0/k$ and $B = \frac{1}{2}\bar{n}\varepsilon_0/k$, but Fig. 1 shows that $\bar{E} = kT^2(\partial \ln Y / \partial T)_{\mu/kT}$ without mathematical approximation gives a better agreement with the observed response.

The partition function yields a distribution of clusters [$P_m = \Delta_m e^{m\mu/kT} / \Gamma$] and a distribution of aggregates [$P_n = \Gamma^n e^{nf\bar{m}\mu/kT} / n! Y$] which we convert into a

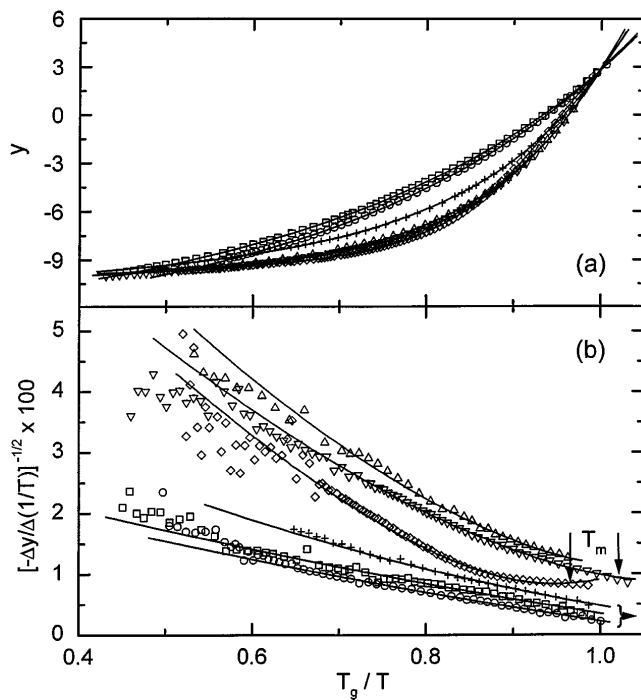


FIG. 1. Symbols are from measurements [3,4] of the inverse peak dielectric loss frequency [$y = -\log(f_p)$] for MT: Δ ; PC: ∇ ; SA: \diamond ; PVAc: $+$; PG: \square ; and GL: \circ . Solid curves are from activation energy of an average aggregate, $y = -\ln(f_0) + |E|/kT$. (a) Plot of y vs T_g/T linearizes the Arrhenius law. "Fragile" liquids show a large amount of curvature, whereas "strong" liquids are more nearly Arrhenius [1]. (b) Plot of $[\Delta y/\Delta(1/T)]^{-1/2}$ vs T_g/T linearizes the VTF law. Fragile liquids show deviations from the VTF law which can be attributed to a transition (arrows) near $T_m \approx T_g$, whereas the strong liquids (which have been offset for clarity) have $T_m < 0.8T_g$.

distribution of relaxation times. Let $P_N \approx P_n P_m$ be the probability of finding an aggregate containing a total of $N = n(1+f)m$ particles. Because each aggregate is a separate system of indistinguishable clusters, it is reasonable to assume that the relaxation rate depends only on the total number of particles in the aggregate, w_N . Thus the susceptibility as a function of frequency (ν) is

$$\chi'(\nu) - i\chi''(\nu) = \Phi_0 \sum_{N=1}^{\infty} NP_N \frac{1}{1 + i2\pi\nu/w_N}, \quad (4)$$

where Φ_0 is a constant amplitude prefactor. The relaxation rate is given by the normal thermal fluctuations in the activation energy about its average value $|\bar{E}|$ [5],

$$w_N = 2\pi\nu_0 e^{-|\bar{E}|/kT} \exp(\bar{C}_p/k/2N), \quad (5)$$

where ν_0 is a constant frequency factor and \bar{C}_p is the heat capacity of an average aggregate. Note that, to a first approximation, the *inverse* size dependence in the "inverse Arrhenius" term yields the usual result that small aggregates relax faster than large aggregates, but because \bar{E} is not extensive, the mechanism is not the usual size-dependent activation energy. Instead, small aggregates have large thermal fluctuations which are activated by

a broad spectrum of excitations, whereas large aggregates require more precisely matched activation energies. Qualitatively, the inverse size dependence converts a relatively symmetric size distribution into the observed asymmetric spectrum of response, while the inverse Arrhenius factor gives the excess response on the high-frequency side of the peak. Quantitatively, this w_N yields superior agreement with the measured dielectric response of supercooled liquids, Fig. 2, with \bar{C}_p as the only temperature-dependent parameter governing the width and shape of the response. The agreement extends well into the high-frequency wing, where all simple empirical formulas such as the KWW law fail.

The inset of Fig. 2 shows a comparison between the average specific heat per particle deduced from dielectric spectra, \bar{C}_p/\bar{N} , and the measured excess specific heat per molecule, Δc_p . Good quantitative agreement is obtained by multiplying \bar{C}_p/\bar{N} by a rational constant which presumably gives the number of particles (binary degrees of freedom) per molecule. All but one of the nonpolymeric systems we have examined have three particles per molecule, while PVAc requires six monomers

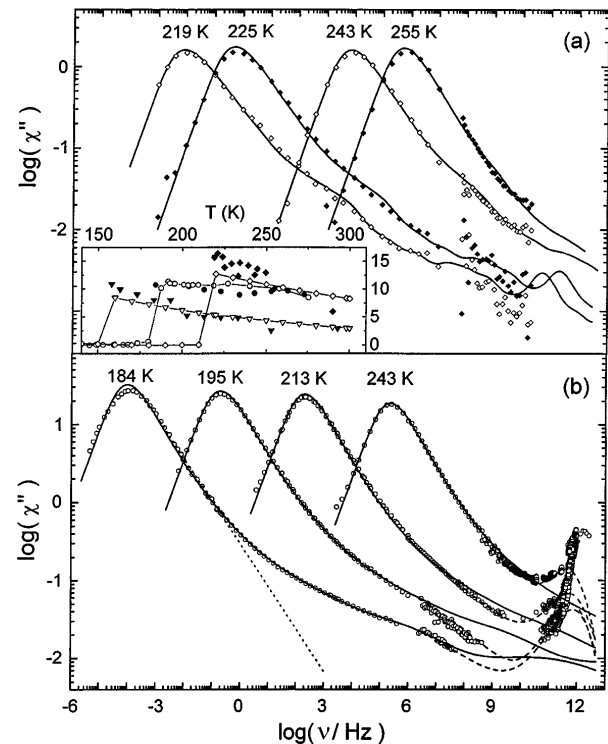


FIG. 2. Frequency-dependent dielectric loss of (a) salol [6] and (b) glycerol [7]. The solid curves give the theoretical response from Eqs. (4) and (5). The dashed curves in (b) include a cutoff in the number of isolated free particles and a resonance at the frequency corresponding to the average energy of each cluster (E_m/h). The dotted line in (b) represents the high-frequency behavior of the KWW law. The inset shows the measured excess specific heat per molecule [8,9] $\Delta c_p/k$ (open symbols with connecting lines), and 3 times the specific heat per particle $3(\bar{C}_p/\bar{N})/k$ deduced from the dielectric response of salol: \blacklozenge ; glycerol: \bullet ; and PC: \blacktriangledown .

to achieve the same 3 degrees of freedom. Thus PVAc at $T = 315$ K has $\bar{N} \approx 600$ particles, corresponding to about 1200 monomers. Assuming spherical aggregates this yields an average dynamical correlation radius of 3.3 nm, consistent with 3 ± 1 nm [12] and 5 ± 2 nm [13] from recent measurements.

The average cluster size \bar{m} and average aggregate size \bar{n} define *two* distinct size scales which correspond to the two distinct energy scales (kT_0 and kB) in the VTF law. We propose the following interpretation. Because energy-reducing fluctuations are intensive, aggregates subdivide into multiple clusters to decrease the net energy; and because only nearby clusters can exchange particles rapidly enough to be indistinguishable, aggregates remain finite sized to increase the net entropy. The transient nature of the clusters implies that they coincide with subtle changes in the position or motion of the particles which induce a relatively strong interaction over a sufficient range to allow use of the mean-field approximation. A possible mechanism is for neighboring molecules in the cluster to reside at or near the most favorable separation for chemical bonding, which sharply strengthens their energy of interaction. We speculate that aggregates are regions of thermodynamic correlation (consistent with NSHB), while clusters are regions of quantum-mechanical coherence [consistent with the secondary response above 10^9 Hz in Fig. 2(b)], but the final picture will require further investigation.

We summarize by comparing our approach to some other theories of supercooled liquids. Two prevalent models for the VTF law are the Adam-Gibbs (AG) [15] theory of cooperatively rearranging regions, and the Cohen-Grest (CG) [16] free-volume theory for percolation of solid clusters in a liquid matrix. Like the CG theory, we consider partially ordered clusters surrounded by a fraction of free particles, but we assume that f is constant and that the transition occurs within the clusters. Furthermore, the CG theory yields first-order-like behavior which must be heterogeneously broadened, whereas our theory is for a second-order transition which is broadened by finite-size effects. The CG theory also gives KWW-like behavior, but with $\beta > \frac{2}{3}$, while most supercooled liquids have $\beta < \frac{2}{3}$. Like the AG theory, we consider size-dependent relaxation rates, but because the energy of mesoscopic clusters is intensive, Eq. (5) gives w_N that varies exponentially with the *inverse* size. Furthermore, the AG theory yields cooperative regions at T_g containing only 4–8 molecules [17]. More realistic correlation lengths of 2–7 nm have been obtained by considering thermal fluctuations within correlated volumes of cooperative regions [18,19], much like the two distinct size scales in our aggregates of clusters. However it is usually assumed that all correlated volumes at a given temperature have the same size, so that energy fluctuations alone are responsible for the spectral width, but at T_g the observed spectral *shape* would require asymmetric energy fluctuations of at least 100 K. Much recent interest in the dynamics

of supercooled liquids has come from the mode-coupling theory [20] that predicts KWW-like behavior at low frequencies, excess loss at high frequencies, and a dynamic transition at a critical temperature (T_c) which is 20–50 K above T_g . Our theory offers an alternative explanation for the critical behavior above T_g in salol [21] and PC [22] where $\varepsilon_0/k \approx T_c$, and explains why the critical behavior is less obvious in glycerol [23] and PVAc [24] where $\varepsilon_0/k < T_g$. Moreover, our theory yields a heterogeneous distribution of relaxation rates, with correlation lengths that are consistent with experiment. Although the basic model presented here gives relatively good agreement with observed VTF- and KWW-like responses, the dashed curves in Fig. 2(b) show how the agreement at very high frequencies can be improved by including resonances and single-particle effects. Finally, since similar responses are found in a wide variety of materials [5], the mesoscopic mean-field theory may ultimately be adapted to many systems.

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