

Mean-field theory, mode-coupling theory, and the onset temperature in supercooled liquids

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We consider the relationship between the temperature at which averaged energy landscape properties change sharply (T_o) and the breakdown of mean-field treatments of the dynamics of supercooled liquids. First, we show that the solution of the wave vector dependent mode-coupling equations undergoes an ergodic-nonergodic transition consistently close to T_o . Generalizing the landscape concept to include hard-sphere systems, we show that the property of inherent structures that changes near T_o is governed more fundamentally by packing and free volume than potential energy. Lastly, we study the finite-size random orthogonal model (ROM), and show that the onset of noticeable corrections to mean-field behavior occurs at T_o . These results highlight connections between the energy landscape and mode-coupling approach to supercooled liquids, and identify which features of the relaxation of supercooled liquids are properly captured by mode-coupling theory.

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The slow dynamics that supercooled liquids undergo as they approach the glass transition has defied a satisfying explanation for many decades [1,2]. Several theoretical paradigms have been presented that shed light on certain features of these dynamics. The notion of an energy landscape has been useful for understanding thermodynamic properties of the glassy state as well as for rationalizing the connection between transport properties and the packing structures associated with local potential energy minima (“inherent structures”) that are visited at a given temperature [2,3]. Other theories, such as mode-coupling theory (MCT) [4,5], have also been influential in explaining the sequence of relaxation events that occurs in mildly supercooled liquids. While successful in several contexts, both the landscape and MCT approaches suffer from problems that limit their utility. The landscape picture does not provide a predictive, quantitative framework for describing the dynamics of supercooled liquids. Furthermore, it is not clear how one could apply energy landscape concepts in a useful way to entropically dominated glassy systems such as hard-sphere liquids. MCT does provide such a framework, but several important predictions made by this theory, including the thermodynamic location of the ergodic-nonergodic transition, are incorrect [6]. Here we elucidate connections between these two viewpoints that shed new light on various features of these seemingly different approaches.

Effort has been made to connect the intuitively based landscape picture to the more mathematical mode-coupling approach. Pioneering work of Kirkpatrick, Wolynes, and Thirumalai [7,8] showed that the mode-coupling equations are exact for certain mean-field spin glasses. In particular, the $p=3$ p -spin model exhibits a dynamical transition at a temperature T_c and a thermodynamic transition at a lower temperature T_K [9–12]. The temperature T_c is associated with a mean-field divergence of barriers, leading to nonergodicity. It has been argued that effects beyond the mean-field limit render the barriers at T_c finite [9,13]. Thus, T_c corresponds to the temperature at which activated processes over finite-sized barriers dominate transport. Since MCT in its simplest form neglects these activated processes, the full wave vector dependent MCT equations exhibit a “glass” transition at T_c

$>T_g$ where T_g is the calorimetric glass transition observed in the laboratory. Several computer studies have attempted to strengthen the connection between activated processes on the energy landscape and the temperature T_c [3,14–16]. Recently, however, simulations have shown that activated processes strongly influence transport in supercooled liquids at temperatures significantly in excess of T_c [17–19]. Thus, the physical meaning and relevance of T_c for finite-dimensional, non-mean-field glassy systems remains unclear.

Several years ago, Sastry *et al.* [3] pointed out the existence of another characteristic landscape temperature, the “onset” (or “landscape influenced”) temperature T_o . T_o may be significantly larger than T_c as calculated by power-law fits of diffusive data, and coincides with the onset of nonexponential and non-Arrhenius relaxation in supercooled liquids. Sastry *et al.* [3] found that T_o also marked the temperature at which averaged energy landscape properties (such as the average value of the inherent structure energy) show a sharp change as a function of temperature. While much work has focused on understanding the qualitative changes in dynamics near T_c , very little work has been devoted to understanding the meaning of T_o . Here we demonstrate connections between MCT (and mean-field-like approaches in general), and the changes in landscape properties that occur as the system is cooled below T_o .

It has long been known that the location of the temperature at which the full wave vector dependent MCT equations predict a loss of ergodicity is significantly higher than T_c as obtained by power-law fits of the temperature dependence of transport coefficients. Here we show that the ergodic-nonergodic transition actually occurs close to T_o . We solve the wave vector dependent MCT equations for the 2×2 matrix $\ddot{\mathbf{F}}(\mathbf{q}, t)$ with matrix elements $F_{ij}(\mathbf{q}, t)$, where [6]

$$\ddot{\mathbf{F}}(\mathbf{q}, t) + \mathbf{\Omega}^2(\mathbf{q})\mathbf{F}(\mathbf{q}, t) + \int_0^t d\tau \mathbf{M}(\mathbf{q}, t - \tau)\dot{\mathbf{F}}(\mathbf{q}, \tau) = 0. \quad (1)$$

The frequency matrix $\mathbf{\Omega}^2(\mathbf{q})$ is defined as

$$[\mathbf{\Omega}^2(\mathbf{q})]_{ij} = \frac{\mathbf{q}^2 k_B T x_i}{m_i} \sum_k \delta_{ik} [\mathbf{S}^{-1}(\mathbf{q})]_{kj} \quad (2)$$

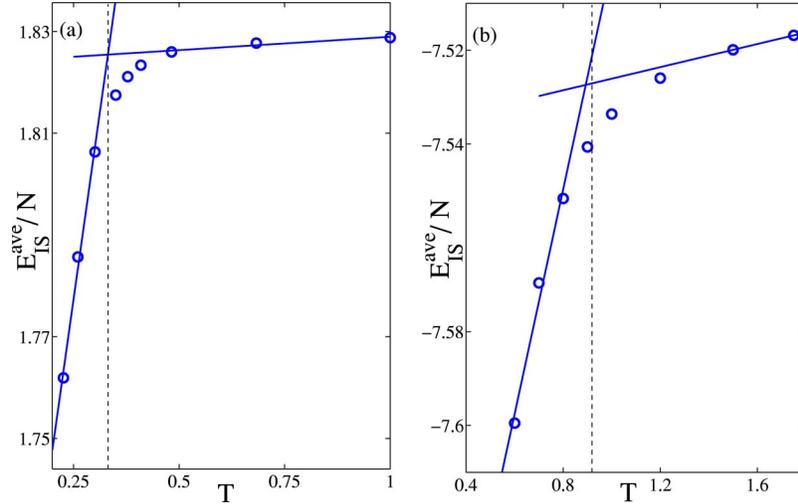


FIG. 1. Average inherent structure energy vs temperature for (a) 70 particle 50/50 soft-sphere system at unit density and (b) 120 particle 80/20 LJ (Lennard-Jones) system at density 1.2. The solid lines are straight line fits to high and low temperature slopes. T_o is defined to be the temperature where these lines cross. The vertical dashed line indicates the temperature of the ergodic-nonergodic transition as calculated by Eqs. (1)–(3). T_c , as calculated by fits to diffusive data, is found to be $T_c=0.246$ for the soft-sphere system and $T_c=0.435$ for the LJ system. Lennard-Jones units are used here and throughout the text.

and the mode-coupling approximation for the memory function is given by

$$M_{ij}(\mathbf{q}, t) = \frac{k_B T}{2n m_i x_j} \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{\alpha\beta} \sum_{\alpha'\beta'} V_{i\alpha\beta}(\mathbf{q}, \mathbf{k}) V_{j\alpha'\beta'} \times (\mathbf{q}, \mathbf{q}-\mathbf{k}) F_{\alpha\alpha'}(\mathbf{k}, t) F_{\beta\beta'}(\mathbf{q}-\mathbf{k}, t), \quad (3)$$

where n is the particle density, x_i and m_i are, respectively, the concentration and mass of particle type i , and $\mathbf{S}(\mathbf{q})$ is the 2×2 matrix of partial structure factors. Expressions for the vertices $V_{i\alpha\beta}$ can be found in the literature [6].

Solving Eqs. (1)–(3) yields the location of the temperature at which the function $F(\mathbf{k}, t)/S(k)$ fails to decay to zero as $t \rightarrow \infty$. In Fig. 1 we plot the average inherent structure (IS) energy $[\bar{E}_{IS}(T)]$ as a function of temperature for two different potentials. The first system studied is the 50/50 soft-sphere mixture studied by Barrat *et al.* [20]. The second system is the 80/20 Lennard-Jones mixture studied by Kob and Andersen [21]. The onset temperature T_o is located where $\bar{E}_{IS}(T)$ show a sharp decrease as a function of temperature, or where the first-order polynomial fits to the high and low temperature data cross. A dashed line indicates the location of the ergodic-nonergodic transition temperature obtained from Eqs. (1)–(3). Clearly, the location of the ergodic-nonergodic transition occurs very close to the landscape onset temperature T_o and not T_c as calculated by fits to diffusion data. Since MCT may be viewed as a particular type of dynamical mean-field theory, the coincidence of the breakdown of MCT at T_o signals the failure of MCT to capture specific non-mean-field effects. The nature of this failure is discussed below.

A particularly troubling feature of energy landscape theories is the inability to treat hard-sphere systems, where barrier crossing events are completely entropic in nature. In or-

der to address this issue, we generalize the inherent structure concept in a manner similar to that discussed by Santen and Krauth [22]. Specifically, we study a binary hard-sphere system consisting of 225 particles with $\sigma_1=0.1$ and 25 particles with $\sigma_2=0.5$ at various packing fractions η [23]. Starting with well equilibrated configurations generated at a given packing fraction, the system is “crunched” until hard-sphere overlap occurs. Some Monte Carlo moves are made during this process to ensure the system reaches a stable packing structure. The final, stable configuration obtained from this procedure is called an inherent structure. In Fig. 2(a) we show the average inherent structure volume $[\bar{V}_{IS}(\eta)]$ versus packing fraction for the binary hard-sphere system. Remarkably, an onset packing fraction η_o may be defined from the inherent structures that again coincides with the ergodic-nonergodic critical packing fraction as found from Eqs. (1)–(3). This not only demonstrates the robustness of the correlation between the dynamics of the ergodic-nonergodic transition as found directly from MCT via Eqs. (1)–(3) and the onset temperature (packing fraction) T_o (η_o), but it also hints at a deep connection between inherent structures labeled by potential energy and configurations defined by packing and free volume. To strengthen this connection, we reconsider a thermal system, namely, the soft-sphere system studied in Fig. 1. Using a crunching procedure (with an upper energy cutoff) similar to that used in the hard-sphere system, we calculate $\bar{V}_{IS}(T)$ versus T . In Fig. 2(b) we show that the onset temperature for changes in $\bar{V}_{IS}(T)$ coincides with T_o as extracted from inherent structure energies $[\bar{E}_{IS}(T)]$ for the same system. This demonstrates that the changes in the inherent structures that are sampled in the liquid range where dynamics become nonexponential are associated with sharp changes in free volume and structural packing motifs. In fact, such quantities are more fundamental

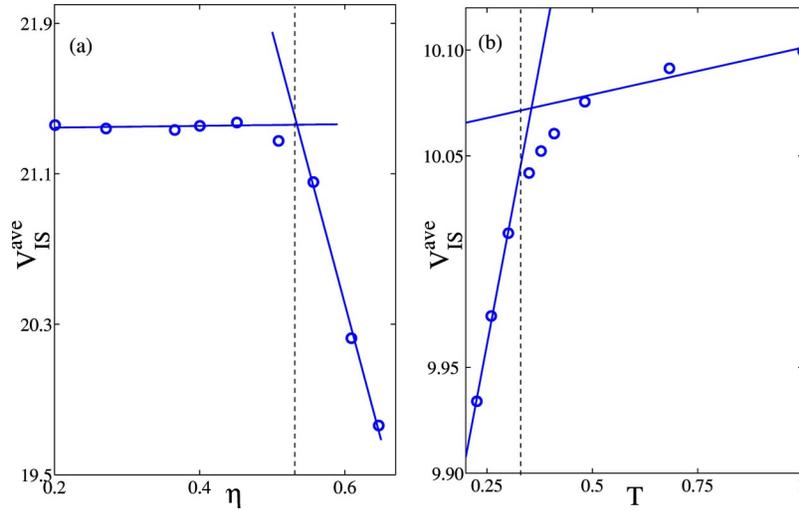


FIG. 2. (a) Average “inherent structure” volume vs packing fraction for the hard-sphere mixture as calculated by the “crunching” procedure described in the text. The dashed line indicates the location of the ergodic-nonergodic transition as calculated from Eqs. (1)–(3). (b) Crunching procedure applied to the soft-sphere system. An energy cutoff has been employed to define the final IS volume. The dashed line indicates the temperature of the ergodic-nonergodic transition as calculated by Eqs. (1)–(3). T_o in this system as defined via $\bar{E}_{IS}(T)$, $T_o^E=0.332$ [see Fig. 1(a)], agrees well with that extracted from the $\bar{V}_{IS}(T)$ definition, $T_o^V=0.356$.

than the quenched potential energy and allow for the generalization of landscape concepts to athermal systems such as hard spheres.

Despite the fact that the solution to the full set of Eqs. (1)–(3) yields an ergodic-nonergodic transition temperature that is very close to T_o , one still expects MCT to give physically sensible results in the range $T_c < T < T_o$. Indeed, Kob *et al.* have demonstrated that Eqs. (1)–(3) accurately account for dynamics at these temperatures if the static input is calculated at a higher (effective) temperature [24], and many of the scaling predictions of MCT appear to be corroborated via computer simulations in this range [25,21]. Indeed, one expects that, in the range $T_c < T < T_o$, the MCT scenario is still sensible but is modified by non-mean-field effects. This possibility is discussed below.

The freezing of $F(\mathbf{k},t)/S(k)$ at T_o (and not T_c) merely signals the *sensitivity* of MCT to changes in the packing structure of the liquid and hints at the breakdown of the mean-field-like approximation that is inherent in the idealized version of mode-coupling theory. To get a better feeling for the nature of this breakdown, we consider the dynamics of the random orthogonal model (ROM) [26]. Specifically, we take the Hamiltonian

$$H = -2 \sum_{ij} J_{ij} \sigma_i \sigma_j, \quad (4)$$

where $\sigma_i = \pm 1$ are Ising spin variables, and J_{ij} is an $N \times N$ random symmetric orthogonal matrix with $J_{ii} = 0$. The Glauber algorithm [27] is employed for dynamics. For $N \rightarrow \infty$, this model is in the same dynamical universality class as the $p=3$ spherical p -spin model. Thus, in this limit, MCT is exact. For N finite, $1/N$ corrections to the MCT should appear. Here, finite N represents the introduction of a finite correlation length (the system size), similar to what would

result in, for example, the $p=3$ spin glass model with finite ranged interactions [29,28]. It has already been shown that for finite N , the model defined by Eq. (4) behaves similar to real liquids, exhibiting landscape properties very similar to atomistic models, as well as nontrivial dynamical properties such as Nagel scaling [30]. In Fig. 3(a) a plot of $\bar{E}_{IS}(T)$ versus T is shown for a particular value of N . The generic features of this plot are not sensitive to N over a wide range of values for finite N . An onset temperature $T_o \approx 0.72$ is found for this model, while $T_c = 0.536$ and $T_K = 0.26$. In Fig. 3(b), we plot $\chi_{N,N'}(T) = \int_0^\infty dt |C_N(t) - C_{N'}(t)|$, where $C_N(t) = (1/N) \sum_{i=1}^N \langle \sigma_i(t) \sigma_i(0) \rangle$ is the disorder-averaged spin-spin correlation function for a finite N system. Clearly, this “susceptibility” measures finite N corrections to mean-field dynamics for $N', N < \infty$. In Fig. 3(b), we plot $\chi_{N,N'}(T)$ versus T for several different choices of N and N' . Remarkably, $\chi(T)$ sharply increases from zero very close to T_o . This result is not sensitive to N and N' for a wide range of values. Indeed, this result demonstrates that noticeable corrections to mean-field (MCT) dynamics occur at $T_o > T_c$ as calculated by fits to transport coefficients.

To determine which portion of the dynamics is sensitive to finite N effects, we have calculated $C_N(t)$ for several different values of N for one particular temperature in the range $T_o > T > T_c$. The intermediate time (“ β -relaxation”) regime is not strongly N sensitive, while the long-time (“ α -relaxation”) regime shows strong finite N effects. This observation is consistent with a recent study of the dynamics of the finite-sized random energy model by Arous *et al.* [31]. These authors have demonstrated that dynamical effects beyond the mean-field limit occur at long times, and that the longest time behavior is compatible with the predictions of the phenomenological trap model [32]. Recent computer simulation work has also shown that the long-time dynamics of atomistic liquids is consistent with an activated trap

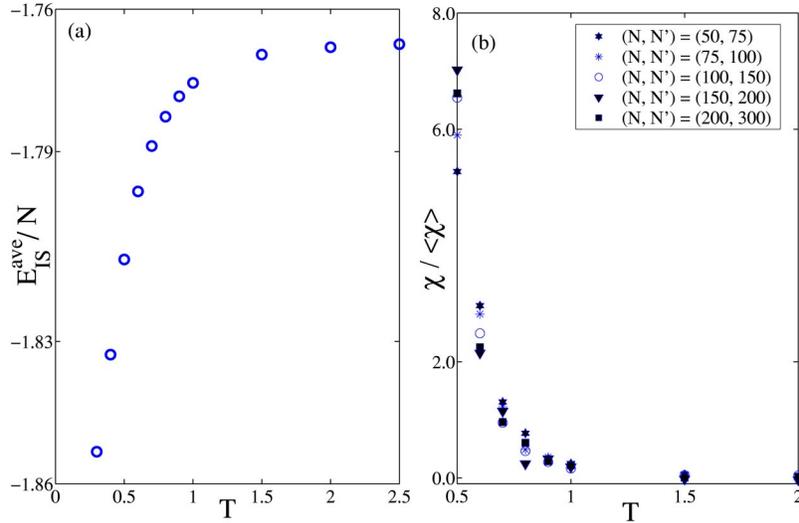


FIG. 3. (a) Average inherent structure energy vs temperature for the ROM model, $T_o = 0.72$. (b) $\chi_{N,N'}(T)/\langle\chi_{N,N'}(T)\rangle$ vs T , where the angular brackets represent an average over all T . Curve fitting similar to that of previous figures yields an approximate onset temperature of non-mean-field effects of $T = 0.735$.

model precisely in the range $T_o > T \geq T_c$. Note that in the ROM model, for finite N, N' , $\chi_{N,N'}(T)$ essentially varies continuously through T_c but changes sharply near T_o . Metabasin dynamics in atomistic simulations also show a sharp onset of traplike behavior near T_o , and continuous variation near T_c [17–19]. It should also be noted that recent work by Berthier and Garrahan on kinetic facilitated models also demonstrates that activated processes set in at T_o , where local dynamical heterogeneities begin to occur [33].

In this paper, we have studied a number of model systems and demonstrated connections between mean-field theory, mode-coupling theory, and the landscape paradigm. The picture that emerges from this work and previous studies is that T_o marks the edge boundary for significant barriers that result from a non-mean-field smearing of the dynamical transition that occurs at T_c in mean-field systems. Barriers that would be infinite at T_c for an infinite-dimensional liquid become finite, and influence dynamics *not just in the vicinity of T_c but at temperatures up to T_o* . Transport involves activation over these barriers, and is traplike at very long times.

What, then, can one expect from the idealized version of MCT? The analog between $1/N$ corrections to mean-field behavior in truncated mean-field spin glasses and corrections to the idealized MCT suggest that MCT should *always* yield quantitative results for the β -relaxation regime. The remarkable scaling predictions of MCT in this regime should be unaffected by the mean-field nature of the approximations inherent in the MCT approach [25]. While MCT is able to account for properties such as time-temperature superposition in the long-time α -relaxation regime, finite corrections to MCT should be noticeable here. These corrections are connected to activated (trap-like) behavior that occurs in the range $T_o > T$. Note that the Gaussian trap model also displays time-temperature superposition in the α -relaxation regime. Clear signs of dynamic heterogeneities occur in simu-

lations for temperatures in the range $T_o > T \geq T_c$ [34]. This *localized* heterogeneous motion is likely connected to activated, trap-like behavior. Our results are thus in harmony with recent studies [35,36], which suggests that the window $T_c < T < T_o$ is a crossover region that contains both MCT and activated behavior.

While we have shown in this work that there are interesting physical connections between the temperature T_o and the breakdown of mean-field theory that have not been previously discussed, an open question still remains regarding the nature of T_c as a dynamical crossover temperature. It is instructive to note that in the p -spin model, T_c and T_o lie very near each other. Non-mean-field effects tend to push these temperatures apart. A scaled parameter $\tau = (T_o - T_c)/T_c$ may provide a measure of how strong the corrections to mean-field behavior are. In the binary soft-sphere mixture of Barrat *et al.* at unit density $\tau \approx 0.25$ while for the Lennard-Jones mixture of Kob and Andersen studied at unit density $\tau \approx 1$. Interestingly, dynamical effects such as the appearance of prominent “hopping” peaks in the van Hove correlation function $G(r, t)$ [37] and short-time secondary maxima in the non-Gaussian parameter $\alpha_2(t)$ and the nonlinear susceptibility $\chi_4(t)$ occur near T_c for the soft-sphere mixture but not for the Lennard-Jones system [38]. Perhaps remnants of the behavior expected at T_c are only noticeable in systems with small τ values that are in some sense closer to idealized mean-field systems [39]. Furthermore, it would be interesting to determine if the value of τ decreases as the physical dimension of the system increases. A systematic study of such open questions is underway.

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