Role of Structure and Entropy in Determining Differences in Dynamics for Glass Formers with Different Interaction Potentials

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We present a study of two model liquids with different interaction potentials, exhibiting similar structure but significantly different dynamics at low temperatures. By evaluating the configurational entropy, we show that the differences in the dynamics of these systems can be understood in terms of their thermodynamic differences. Analyzing their structure, we demonstrate that differences in pair correlation functions between the two systems, through their contribution to the entropy, dominate the differences in their dynamics, and indeed overestimate the differences. Including the contribution of higher order structural correlations to the entropy leads to smaller estimates for the relaxation times, as well as smaller differences between the two studied systems.

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Many approaches toward understanding the dynamical behavior of liquids attempt to predict dynamics in terms of static structural correlations [1,2], often focussing on two-body correlation functions. In turn, it has been argued that the short range, repulsive interactions have a dominant role in determining the pair correlation function, with the attractions making a perturbative contribution. Such an approach was shown to be effective in predicting the pair correlation function for dense liquids interacting via the Lennard-Jones (LJ) potential, by Weeks, Chandler, and Andersen, who treated the LJ potential as a sum of a repulsive part (referred to subsequently as the WCA potential) and the attractive part [3]. If such a treatment carries over to the analysis of dynamics, the expectation would be that liquids with LJ and the corresponding WCA interactions should have similar dynamics. However, in a series of recent papers, Berthier and Tarjus have shown that model liquids with LJ and WCA interactions, exhibiting fairly similar structure, exhibit dramatically different dynamics, characterized by a structural relaxation time, at low temperatures [4–7]. In order to analyze this "non-perturbative" effect of the attractive forces on the dynamics, Berthier and Tarjus studied a number of "microscopic" approaches to predict the dynamics, based on knowledge of the static pair correlations. They conclude that the approaches they analyze are unsuccessful in capturing the differences in dynamics between the LJ and WCA systems. Dyre and co-workers [8–10] have argued that the origins of these observations are not specifically in the inclusion or neglect of attractive interactions [10], but in factors such as the inclusion of interactions of all first shell neighbors [8], and the presence or absence of scaling between systems or state points compared [9]. In particular, Pedersen and Dyre [9] identify a purely repulsive inverse-power-law (IPL) potential that has dynamics that can be mapped to the LJ case studied by Bertheir and Tarjus. These observations notwithstanding, the inability to capture the differences between the LJ and WCA systems highlighted by Berthier and Tarjus by predictive approaches to dynamics remains an open issue. In this regard, it has been suggested by Coslovich [11,12] that higher order structural correlations may play a significant role in determining dynamics, and he argues this point by showing that the temperature variation of locally preferred structures for the LJ and WCA systems tracks that of the relaxation times [11]. Hocky *et al.* [13] show, by evaluating the point-to-set length scales in the LJ, WCA, and IPL liquids, that while the LJ and IPL liquids show essentially the same temperature dependence, the WCA system differs from these two, thereby offering a quantitative explanation of the dynamics, in terms of a quantity that has implicit dependence on two-body and many body structural correlations.

Among the prominent predictive relationships between equilibrium properties and dynamics for liquids at low temperatures is the Adam-Gibbs relation [14]

$$\tau(T) = \tau_o \exp\left(\frac{A}{TS_c}\right), \tag{1}$$

which expresses relaxation times τ in terms of a thermodynamic quantity, the configurational entropy S_c. The random first order transition theory [15], which relates relaxation times to a growing static length scale for activation, $\tau \sim \exp(\xi^{\psi}/k_B T)$, with the static length [13] depending on S_c as $\xi \sim S_c^{1/(d-\theta)}$ (d is the spatial dimensionality, and θ is an exponent related to interface energy), leads to the Adam-Gibbs relation for suitable values of exponents θ and ψ [16,17]. The usefulness of the Adam-Gibbs relationship in comprehending the differences in dynamics of the LJ and WCA systems has not been hitherto explored.

In this Letter, we test whether the differences in the interaction potential between the LJ and WCA systems, while having a modest effect on structure, have a more significant effect on the thermodynamics, and the Adam-Gibbs (AG) relation can hence capture the quantitative differences in the dynamics between these systems. We further employ this relation as a tool to explore the contributions of two-body and higher order structural correlations, by considering a two-body approximation to the configurational entropy. We find the following: (1) The Adam-Gibbs relationship quantitatively captures the differences in the dynamics between the LJ and WCA systems. (2) Two body correlations alone, used to obtain an approximation to the configurational entropy, yield a significant difference in predicted relaxation times, indeed overestimating the difference, indicating a strong sensitivity to changes in pair correlations. Reminiscent of the predictions from mode coupling theory (MCT) calculations, however, the relaxation times are significantly overestimated using only the two-body approximation to the entropy. We note, however, that the AG relation is based on activated dynamics unlike the MCT, and based on two-body correlations alone, captures the difference between the LJ and WCA systems under conditions when the MCT fails to do so [5], such as at high densities [18]. (3) Multiparticle correlations are essential to correctly compute the configurational entropy S_c in order for the Adam-Gibbs relation to capture the dynamics accurately. The residual multiparticle entropy (RMPE), arising from many particle correlations, speeds up the dynamics at low temperatures and is larger for the LJ system, which is at odds with the notion that stronger multiparticle correlations are responsible for the stronger temperature dependence of the relaxation times but consistent with the observation that a significant contribution to higher order (three body) correlations arises from the amplification of small differences in correlation at the two-body level [11,12]. We, however, clarify that two-body correlations by themselves predict a more rapid slowing-down of dynamics, and the inclusion of higher order correlations speeds up the dynamics, but only relative to what is predicted by the two-body correlation information.

We study the LJ and WCA versions of the Kob-Andersen binary mixture at $\rho = 1.2$, where the difference in dynamics between the two systems is pronounced [7] with simulation details as in Ref. [7] using LAMMPS simulation code [19]. Lengths, temperatures, and times are given in units of σ_{AA}, ϵ_{AA}/k_B, $(m\sigma_{AA}^2/\epsilon_{AA})^{1/2}$, respectively. We calculate the relaxation time τ from the overlap function $q(t)$ as described in Ref. [20], by the condition $q(t=\tau) = 1/e$.

The temperature dependence of the relaxation times described earlier in Ref. [4] shows that the LJ system has a much stronger temperature dependence than the WCA system. We quantify the temperature dependence by fitting $\tau(T)$ to the Vogel-Fulcher-Tammann (VFT) expression $\tau(T)=\tau_o \exp\{1/[K_{\rm VFT}((T/T_{\rm VFT})-1)]\}$. The resulting kinetic fragilities for the two systems are $K_{\rm VFT}=0.19$ for the LJ liquid and 0.14 for the WCA liquid, with divergence temperatures $T_{\rm VFT}=0.28$ and 0.16, respectively, with the ratio $K_{\rm VFT}^{\rm LJ}/K_{\rm VFT}^{\rm WCA} = 1.36$. The VFT form can be obtained from the AG relation if $TS_c = K_T[(T/T_K) - 1]$, with the kinetic fragility $K_{\rm VFT}$ given in terms of the thermodynamic fragility K_T (with $T_K = T_{\rm VFT}$) by $K_{\rm VFT} = K_T/A$. The configurational entropies (per particle) are calculated as the difference between the total and vibrational entropies, $S_c = S_{\rm total} - S_{\rm vib}$ [21,22]. As shown in Fig. 1(a) the vibrational entropies are similar for the two systems. In the inset of Fig. 1(b) we show that, by extrapolation, S_c for the LJ system vanishes at a higher temperature, and (main panel) has a higher thermodynamic fragility K_T. Figure 1(c) shows the

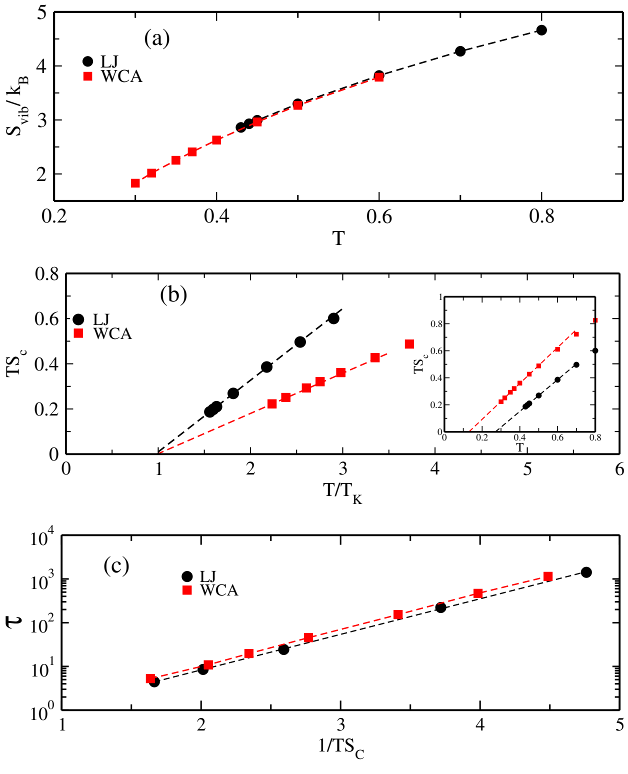

FIG. 1 (color online). (a) The temperature dependence of vibrational entropy ($S_{\rm vib}$) for the LJ and WCA systems. (b) Determination of thermodynamic fragility K_T from the slope of the linear fit. Inset: T_K is the Kauzmann temperature obtained from the linear fit from $S_c(T_K) = 0$. T_K is 0.27 and 0.134 for the LJ and WCA systems, respectively. (c) The Adam-Gibbs plot, showing that the differing temperature dependence of relaxation times is quantitatively captured by the temperature variation of the configurational entropy.

Adam-Gibbs plot, τ vs $1/TS_c$. For both the LJ and WCA systems, the AG relation is not only valid, but the slopes A for the two systems (related to the high temperature activation energy E_∞ and the limiting value of S_c, S_c^∞, by $A = E_\infty S_c^\infty$) are very close. Thus, the temperature variation of the configurational entropy S_c fully captures the differences in the dynamics between these two systems.

In order to discuss the contribution of two-body and higher order static correlations to the dynamics, we consider the per particle excess entropy $S_{\rm ex}$, defined by $S_{\rm total} = S_{\rm id} + S_{\rm ex}$, where $S_{\rm id}$ is the ideal gas entropy (per particle) [22]. $S_{\rm ex}$ can be expanded in an infinite series $S_{\rm ex} = S_2 + S_3 + \cdots = S_2 + \Delta S$ using Kirkwood's factorization [23] of the N-particle distribution function [24–26]. S_n is the "n" body contribution to the entropy. Thus, the pair excess entropy is S_2 and the higher order contributions to excess entropy is given by the RMPE $\Delta S = S_{\rm ex} - S_2$ [27]. S_2 for a binary system can be written in terms of the partial radial distribution functions

$$\frac{S_2}{k_B} = -2\pi\rho\sum_{\alpha,\beta}x_\alpha x_\beta\int_0^\infty\{g_{\alpha\beta}(r)\ln g_{\alpha\beta}(r) - [g_{\alpha\beta}(r) - 1]\}r^2 dr, \qquad (2)$$

where $g_{\alpha\beta}(r)$ is the atom-atom pair correlation between atoms of type α and β, N is the total number of particles, x_α is the mole fraction of component α in the mixture, and k_B is the Boltzmann constant. In Fig. 2 we show a comparison of $S_{\rm ex}$ and S_2. Interestingly, for both the LJ and WCA systems, starting out at high temperatures, being larger than $S_{\rm ex}$ as one may expect, S_2 becomes smaller than $S_{\rm ex}$ at low temperatures. This behavior, previously noted in other contexts [28–30], means that the RMPE, arising from many body effects, is positive at low temperatures. This change in sign in RMPE implies that although many body correlations at high temperature slow down the dynamics as may be expected, at low temperature their role is reversed. Further, we note that the RMPE is at all temperatures bigger for the LJ than the WCA system—thus, the role of many body correlation at low temperatures is to increase the entropy and to a greater extent for the LJ than the WCA system.

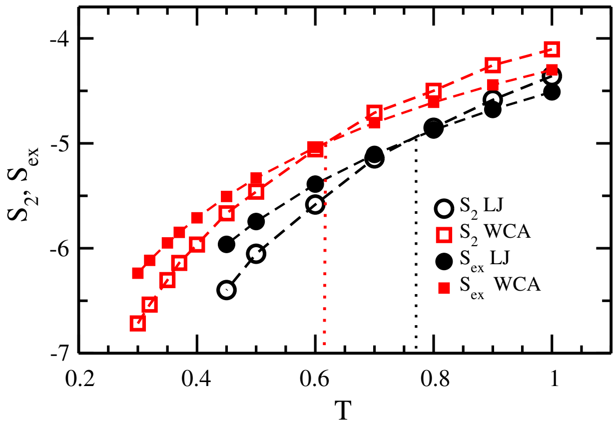

FIG. 2 (color online). Plots of $S_{\rm ex}$ and S_2 versus temperature, showing that the two quantities cross at intermediate temperatures for both models. The crossover temperatures are 0.77 and 0.61 for the LJ and WCA systems, respectively. The dotted lines are a guide to the eye.

At normal liquid temperatures, a semiquantitative correlation between the dynamics (transport properties) and thermodynamics (excess entropy), proposed by Rosenfeld [31,32], has been extensively studied in recent times, with the form $\tau(T) = C\exp[-KS_{\rm ex}]$, where C and K are constants. Since the pair entropy S_2 accounts for 80%–90% of the excess entropy [33] (Fig. 2), many studies replace $S_{\rm ex}$ by S_2 [7,34–37]. For the systems studied here this approximation is found to hold good for high T. We can write

$$\tau(T) = C\exp[-KS_{\rm ex}] = \tau_2^R(T)\exp[-K\Delta S], \qquad (3)$$

where $\tau_2^R(T) = C\exp[-KS_2]$. C and K are obtained from linear fits of $\ln\tau(T)$ against $S_{\rm ex}$ at high temperatures (above the temperatures $T = 0.8$ and 0.6 for the LJ and WCA systems, respectively). The τ_2^R thus obtained, plotted for the LJ and WCA systems in Fig. 3 for high to intermediate temperatures, agree well with $\tau(T)$ since the contribution from ΔS is only about 10% of $S_{\rm ex}$. As shown in the inset of Fig. 3, the ratio of τ values for the LJ and WCA systems are well approximated by that obtained with τ_2^R.

We next turn to the role of two-body and higher order correlations in determining the dynamics as reflected in the configurational entropy. To get an estimate of the configurational entropy as predicted by the pair correlation we rewrite S_c in terms of the pair contribution to the configurational entropy S_{c2}

$$S_c = S_{\rm id} + S_{\rm ex} - S_{\rm vib} = S_{\rm id} + S_2 + \Delta S - S_{\rm vib} = S_{c2} + \Delta S, \qquad (4)$$

where $S_{c2} = S_{\rm id} + S_2 - S_{\rm vib}$. As mentioned earlier the vibrational entropies of the LJ and WCA systems are found to be very close to each other [Fig. 1(a)]. However, the apparently similar structures predict different S_2 (Fig. 2) and S_{c2} values. We obtain the thermodynamic fragilities K_{T2} as predicted by S_{c2} following the same procedure as described for S_c and find the LJ system to be more fragile. Thus, even considering only two-body correlations we find the LJ and the WCA systems to be thermodynamically different. This finding is similar to the observation [12] that significant changes in thermodynamic properties and also higher order correlation functions may arise as a result of amplification of small changes in the pair correlations.

To determine the effect of pair correlations on the low temperature dynamics we estimate the relaxation times as predicted by accounting only for two-body correlations, $\tau_2^{\rm AG}$. To this end, we reexpress the AG relation as follows:

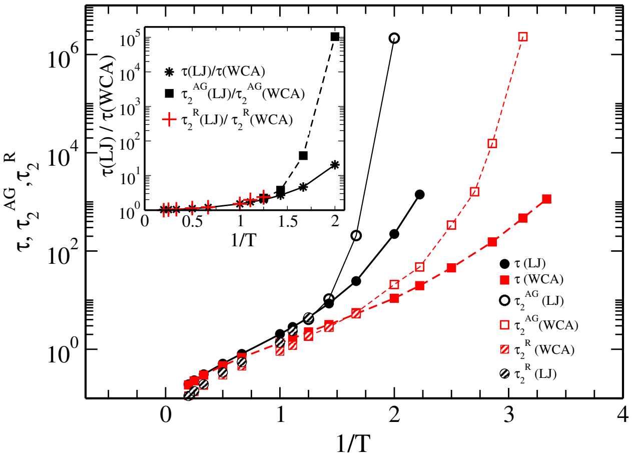

FIG. 3 (color online). τ, τ_2^{AG}, τ_2^R vs $1/T$ for the LJ and WCA systems. Inset: their ratios for the LJ and WCA systems versus $1/T$.

$$\tau(T) = \tau_o \exp\left(\frac{A}{TS_c}\right) = \tau_2^{\mathrm{AG}}(T) \exp\left(-\frac{A * \Delta S}{TS_{c2}S_c}\right), \quad (5)$$

where $\tau_2^{\mathrm{AG}}(T) = \tau_o \exp(A/TS_{c2})$. The τ_2^{AG} for the LJ and the WCA systems are plotted in Fig. 3, as well as their ratio (inset). The τ_2^{AG} diverge at higher temperatures than $\tau(T)$, reminiscent of the behavior of relaxation times according to MCT calculations. However, the τ_2^{AG} for the LJ and WCA systems are widely different, and capture the corresponding differences in $\tau(T)$, unlike relaxation times obtained from the MCT and other microscopic theories, which rely on the pair-correlation function $g(r)$, studied in Ref. [6].

Interestingly, however, the divergence temperatures T_{K2} (the temperature where $S_{c2} = 0$) almost coincide with the MCT divergence temperatures T_c obtained from fits to relaxation times for $\rho = 1.2,1.6$, as shown in Table I. Elucidating the significance of this observation requires further investigations, to be pursued in the future.

As seen in the inset of Fig. 3, the ratio of relaxation times is overestimated by the corresponding ratio of τ_2^{AG}. The kinetic fragility K_{VFT2} as obtained by fitting the temperature dependence of τ_2^{AG} to a VFT form shows that the LJ system is more fragile. Their ratio $K_{\mathrm{VFT2}}^{\mathrm{LJ}}/K_{\mathrm{VFT2}}^{\mathrm{WCA}} = 1.94$ is bigger than 1.36 obtained from $\tau(T)$. Thus, considering only the two-body contribution to the entropy, the Adam-Gibbs relation overestimates the difference in the dynamics between the LJ and WCA systems, rather than failing to capture differences between them, contradicting the expectation that the pair correlation contributions yield similar dynamics, and that the many body correlations may drive the difference between the two systems. Instead, the role of many body correlations, other than lowering the predicted relaxation times for both systems, is also to reduce the predicted difference between them. Although the value of ΔS is similar over the whole temperature regime, it plays a greater role at low temperatures. The crossover temperatures, $T = 0.77$ and 0.61 for the LJ and WCA systems, respectively, demarcate the regime where multiparticle correlations play a significant role, and round off the divergence suggested by the MCT or the AG relation using only two-body correlations.

TABLE I. Comparison of temperatures of diverging relaxation time from MCT fits (T_c) and from the AG relation using the two-body approximation to the entropy (T_{K2}) for densities $\rho = 1.2,1.6$.

	$\rho = 1.2$		$\rho = 1.6$	
	T_c	T_{K2}	T_c	T_{K2}
LJ	0.435	0.445	1.76	1.757
WCA	0.28	0.268	1.69	1.696

The increase in ΔS with decreasing T is usually associated with some ordering in the system [27,36,38], which we now show is also reflected in the pair correlation function. The first peak of the pair correlation function shifts to the right [39] as the temperature decreases, as shown in Fig. 4. Earlier studies have shown that the "A" particles in both the LJ and WCA models show a tendency toward fcc ordering [11,40,41]. As shown in the inset of Fig. 4, the first peak position of the pair correlation function indeed moves toward the value for the fcc lattice as the temperature is lowered.

In summary, we have shown that the temperature dependence of the configurational entropy, via the Adam-Gibbs relation, explains quantitatively the differences in the dynamics between the LJ and WCA systems we study. Using only the two-body correlation information to the configurational entropy, we have shown that these correlations capture the differences in the dynamics between the two systems, indeed overestimating the differences, contrary to the expectation that the similarity of pair correlation functions between the two systems lead to similar predictions for the dynamics. The contributions from the many body correlations speed up the dynamics thus significantly correcting the overestimation of the relaxation times as solely predicted by the

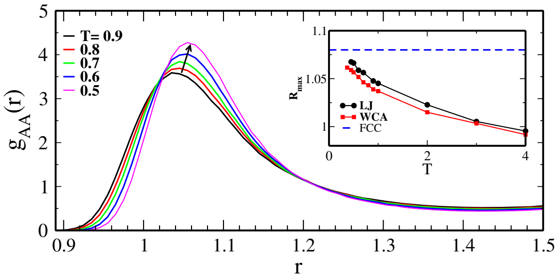

FIG. 4 (color online). The first peak position R_{max} of the radial distribution function shifts to the right with decreasing temperature. Inset: R_{max} moves toward the position of the fcc lattice.

pair correlation information and this effect is found to be more pronounced for the LJ system. How the significant structural changes, captured by pair correlation and higher order structural correlations, may be related to the point-to-set correlation length [13] is an important open question to be addressed in future work.

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