Connection between Adam-Gibbs Theory and Spatially Heterogeneous Dynamics

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We investigate the spatially heterogeneous dynamics in the extended simple point charge model of water using molecular dynamics simulations. We relate the average mass n^* of mobile particle clusters to the diffusion constant and the configurational entropy. Hence, n^* can be interpreted as the mass of the "cooperatively rearranging regions" that form the basis of the Adam-Gibbs theory of the dynamics of supercooled liquids. We also examine the time and temperature dependence of these transient clusters.

More than 35 years ago Adam and Gibbs (AG) proposed a theory to describe the dynamics of supercooled liquids [1,2]. In their approach they suggest that the system changes its configuration by the motion of independent cooperatively rearranging regions (CRR). Their main result is that the diffusion constant D is related to the temperature T and the configurational entropy of the system S_{conf} by

$$D \propto \exp(-A/TS_{\text{conf}}). \tag{1a}$$

In the thermodynamic limit, they interpreted S_{conf} as $k_B \log W_c$, where W_c is the number of configurations accessible by the system and k_B is the Boltzmann constant. More recently, W_c has been interpreted as the number of basins in the potential energy surface (PES) accessible to the system in equilibrium, facilitating direct calculation of S_{conf} by computer simulations [3]. The AG prediction has been tested and appears to be valid across a wide spectrum of liquids [4,5]. The AG theory also hypothesizes a relation between S_{conf} and the characteristic mass z of the CRR. However, the CRR are not precisely defined in the theory, and in the absence of a definition it has been challenging to test this aspect of AG theory.

More recently, computer simulations on simple systems (such as Lennard-Jones mixtures) have shown that particles of high mobility tend to form clusters, and the concept of spatially heterogeneous dynamics (SHD) is evolving [6–14]. Sets of neighboring particles move with enhanced or diminished mobility relative to the average on a time scale intermediate between ballistic and diffusive motion. While there has been interest in the possible relation between clusters obtained from a SHD analysis and the CRR of the AG theory, a link between the quantitative SHD methods and the AG predictions has not been found.

Here we show that on the time scale where SHD is prominent, the average cluster size n^* can be related to the mass z of CRR, thus connecting the quantitative SHD analysis to the qualitative approach of AG. Our results are based on molecular dynamics simulations of the extended simple point charge model of water [15]. We simulate $N = 1728$ molecules at fixed density $\rho = 1.0$ g/cm^3 and a range of T from 200 to 260 K (at 10 K intervals). For each T, we run two independent simulations to improve statistics. We find that D can be fit with

$$D \sim (T - T_{\text{MCT}})^\gamma \tag{1b}$$

using the values for the mode coupling temperature $T_{\text{MCT}} = 193$ K and the diffusivity exponent $\gamma = 2.8$ reported in Ref. [16].

To facilitate comparison with previous work, we use the same approach to define SHD clusters as that employed to study a Lennard-Jones (LJ) mixture [8] and experiments on colloids [14]. We define the mobility of a molecule at a given time t_0 as the maximum displacement of the oxygen atom in the interval $[t_0, t_0 + \Delta t]$. Following Ref. [8], we calculate the self part of the time-dependent van Hove correlation function [17] $G_s(r, t)$ at $t = t^*$, the time at which the non-Gaussian parameter

$$\alpha_2(t) \equiv \tfrac{3}{5}\langle r^4(t)\rangle/\langle r^2(t)\rangle^2 - 1 \tag{2}$$

has a maximum [18]. We fit $G_s(r, t)$ with a Gaussian approximation $G_0(r)$ and define r^* as the second intersection between these distributions. We find r^* is in the range 0.2–0.25 nm for all T. We focus on the fraction ϕ of "mobile" molecules given by $\phi \equiv \int_{r^*}^\infty 4\pi r^2 G_s(r, t^*)dr$, i.e., the average fraction of molecules with a displacement larger than r^* in the interval t^*. Depending on T, we find $6\% < \phi < 8\%$. For simplicity, we fix $\phi = 7\%$ for all T. Similar values of ϕ were found in atomic systems [7,8,14] and in polymer melts [19]. Finally, we define a cluster of mobile molecules at each interval Δt as those mobile molecules whose nearest neighbor oxygen-oxygen distance at time t_0 is less than the first minima of the oxygen-oxygen radial distribution function [20,21].

It appears that the basic features of SHD found for models of simple liquids extend to the more complex

molecular liquid, water. In Fig. 1 we present four snapshots of mobile particle clusters at $T = 210$ K for $\Delta t = t^*$. Particles follow each other in a roughly linearly fashion [7,14]. In LJ systems [7], monoatomic liquids [22], and polymers [23], complex clusters are composed of more elementary "strings," where particles follow each other in a roughly linear fashion. For water, small clusters are indeed stringlike [e.g., Fig. 1(a)], but the molecules conform to the hydrogen bond geometry, and hence the clusters appear to be less linear than clusters found in LJ systems. Clusters become less stringlike as their size increases [7,24], and the fraction of branching points—molecules with more than two neighbors [Fig. 1(b)]—increases with increasing cluster size [Figs. 1(c) and 1(d)].

To relate SHD to the AG approach, we calculate the average cluster mass $\langle n(\Delta t) \rangle$ for each T. In the AG approach to dynamics, the CRR are characterized by the number of particles z and configurational entropy $s_{conf}(z)$ of the CRR; AG argue that $z = N s_{conf}(z)/S_{conf}$. Motivated by the recent finding that the average instantaneous cluster mass scales inversely with the entropy in a model of equilibrium polymerization [25], we use $n^* \equiv \langle n(t^*) \rangle$ as a measure of z, since at t^* correlations are very pronounced and $\langle n(t) \rangle$ is nearly maximal [26]. Using the values of S_{conf} from Ref. [4], we find a linear relationship between

n^* and $1/S_{conf}$ [Fig. 2(a)],

$$n^* - 1 \propto \frac{1}{S_{conf}}. \tag{3}$$

This finding is consistent with the possibility that $n^* - 1$ can be understood as a measure of z and provides a quantitative connection between SHD clusters and the AG approach [27]. It is necessary to subtract one from n^* to obtain direct proportionality, implying that a cluster of unit size does not correspond to a CRR [8]. Equation (3) provides a clear link between a cluster property n^* and a property of the PES, S_{conf}. Since Eq. (1a) relates S_{conf} to D, using Eq. (3) we expect to find

$$D \sim e^{-A(n^*-1)/T}. \tag{4}$$

Indeed, Fig. 2(b) confirms this expectation.

We next address the question of how SHD clusters in water depend on the observation time Δt. We focus on the number average $\langle n(\Delta t) \rangle$ and $\langle n(\Delta t) \rangle_w = \langle n^2(\Delta t) \rangle/\langle n(\Delta t) \rangle$; $\langle n(\Delta t) \rangle_w$, the weight average cluster size, is the average size of a cluster to which a randomly chosen molecule belongs. Figure 3 shows $\langle n(\Delta t) \rangle$ and $\langle n(\Delta t) \rangle_w$ for $T = 210$ K. To eliminate the random contribution, we normalize $\langle n(\Delta t) \rangle_w$ by $\langle n_r \rangle_w$, the weight average cluster size for ϕN randomly chosen molecules. For comparison, we also include the non-Gaussian parameter $\alpha_2(\Delta t)$ and the mean-squared displacement $\langle r^2(\Delta t) \rangle$ [Fig. 3(a)] which
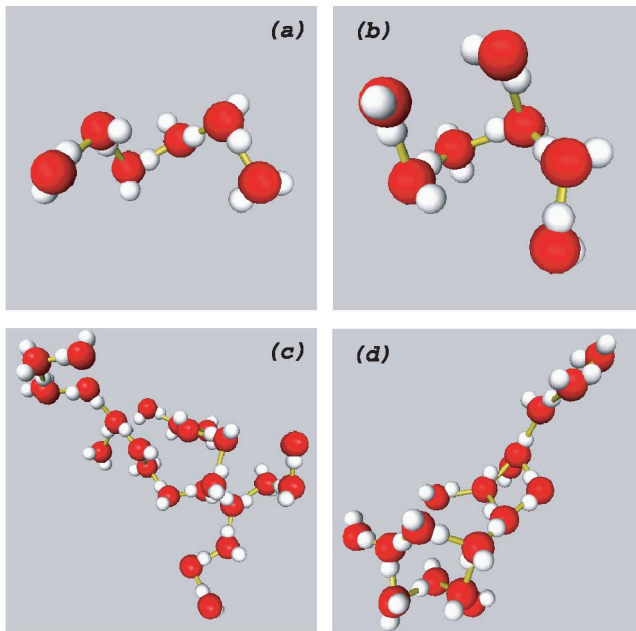

FIG. 1 (color online).   Four clusters of mobile molecules found at $T = 210$ K defined with an observation time $\Delta t = t^*$. Tubes connect neighboring molecules whose oxygen-oxygen distance is less than 0.315 nm, the first minimum in the oxygen-oxygen radial distribution function. Small clusters can be either (a) stringlike or (b) nonstringlike, showing branching points (molecules with more than two neighbors). Larger clusters exhibit more complicated structures, including (c) substrings and (d) loops.
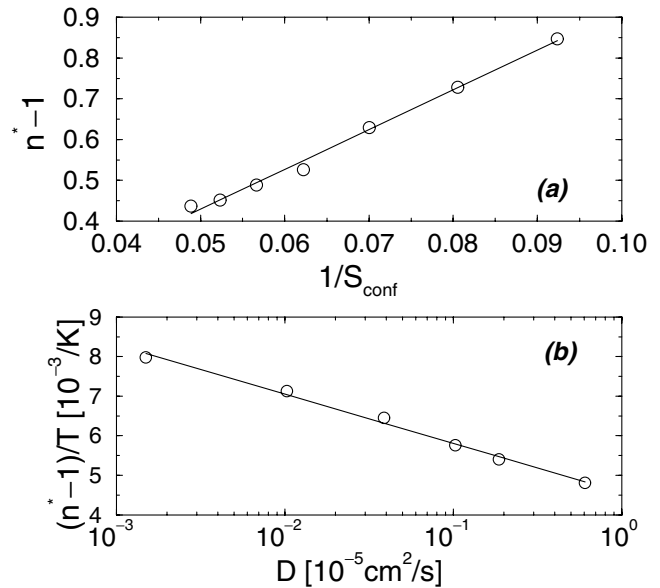

FIG. 2.   (a) The average cluster size n^* is proportional to the inverse of the configurational entropy S_{conf} suggesting that $n^* - 1$ can be used as a measure of the size of the cooperatively rearranging regions hypothesized by Adam and Gibbs. The units of S_{conf} are J/K mol. (b) Log-linear plot of $(n^* - 1)/T$ as a function of the diffusion constant D. The AG prediction $D \sim \exp(A/T S_{conf})$ implies that $\log D \sim (n^* - 1)/T$. This relationship holds for almost three decades in D.

displays the three characteristic time regimes, ballistic, cage, and diffusive.

The behavior of $\langle n(\Delta t)\rangle_w/\langle n_r\rangle_w$ is analogous to that for polymer systems [19], with the exception that there is a clear increase in $\langle n(\Delta t)\rangle_w/\langle n_r\rangle_w$ at the time scale on which molecules go from the ballistic to the cage regime. This additional feature is likely due to strong correlations in the vibrational motion of the first-neighbor molecules, owing to the presence of hydrogen bonds. In Fig. 3(c) we show $\langle n(\Delta t)\rangle_w/\langle n_r\rangle_w$ for all T. For $T \leq 240$ K, the maximum in $\langle n(\Delta t)\rangle_w/\langle n_r\rangle_w$ increases in magnitude and shifts to larger time scales with decreasing T. The plateau at the

crossover from the ballistic regime is nearly T independent, as expected since the mean collision time is nearly T independent. For $T \gtrsim 250$ K, the maximum and the plateau merge, and hence it is not possible to separately distinguish these features.

We find that t^* is slightly larger than t_{max}, the time where the maximum of $\langle n(\Delta t)\rangle_w$ occurs. Both characteristic times correspond to the late-β/early-α time regime of the mode coupling theory (MCT). We find (Fig. 4)

$$t^* \sim (T - T_{MCT})^{-\delta}, \qquad [\delta = 2.7 \pm 0.1] \qquad (5a)$$

and

$$t_{max} \sim (T - T_{MCT})^{-x}, \qquad [x = 2.7 \pm 0.1]. \qquad (5b)$$

The values of δ and x are close to the value of γ, $\gamma = 2.8$. For the LJ polymer melt, simulations show that $x = 1/2a$, where a is the scaling exponent predicted by MCT for the β time scale, suggesting that t_{max} may be a measure of the "elusive" β relaxation time scale [19]. MCT predicts that knowing γ, defined in Eq. (1b), is sufficient for determining a [28]. If t_{max} were a measure of the β time scale, then we would expect $a = 0.28$ [16], and hence x would be equal to 1.78. From Eq. (5b), we see that $x > 1.78$, so t_{max} does *not* provide a measure of the β time scale. Additional tests of the temperature scaling of t_{max} for other liquids are needed to determine the range of liquids for which t_{max} can be considered a measure of the β time scale.
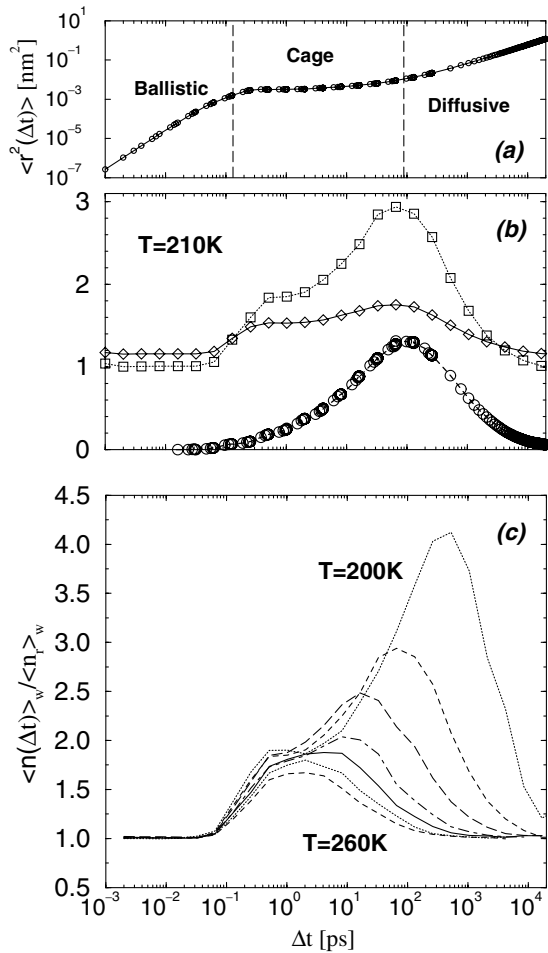

FIG. 3. (a) Mean square displacement $\langle r^2(\Delta t)\rangle$ at $T = 210$ K showing the ballistic, cage, and diffusive regimes (separated by dotted lines). (b) Normalized weight cluster size $\langle n(\Delta t)\rangle_w/\langle n_r\rangle_w$ ($\square$), non-normalized average number of molecules $\langle n(\Delta t)\rangle$ ($\diamond$), and the non-Gaussian parameter $\alpha_2(\Delta t)$ ($\bigcirc$). All three quantities correlate with the two crossovers in $\langle r^2(\Delta t)\rangle$ and the maxima of $\langle n(\Delta t)\rangle_w/\langle n_r\rangle_w$ and $\langle n(\Delta t)\rangle$ occur at times slightly smaller than the time for the maximum in $\alpha_2(\Delta t)$. (c) Weight cluster size $\langle n(\Delta t)\rangle_w/\langle n_r\rangle_w$ for temperatures ranging from 200 to 260 K in intervals of 10 K. Note the T-independent plateau at the crossover from ballistic motion to cage.
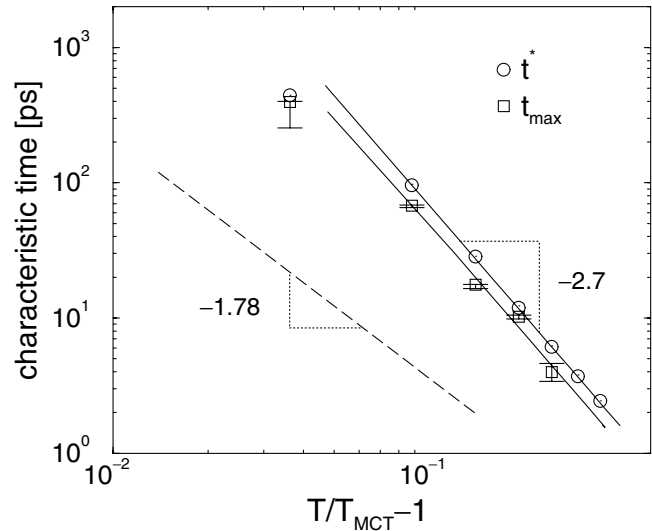

FIG. 4. Temperature dependence of t^* and t_{max}, the times at which the maxima of the non-Gaussian parameter and the weight average cluster size occur. We find $t^* \sim (T/T_{MCT} - 1)^\delta$ and $t_{max} \sim (T/T_{MCT} - 1)^x$, where $x = \delta = 2.7 \pm 0.1$. The expected value of the exponent x, following arguments in [19], is 1.78 (long-dashed line). The values of t^* and t_{max} for $T = 200$ K were not included in the fits because 200 K is too close to $T_{MCT} = 193$ K (deviations from MCT are known to occur as $T \rightarrow T_{MCT}$).

In summary, the relation we find between n^* and S_{conf}, Eq. (3), provides a link between SHD and properties of the PES [29]. In the context of AG theory, our findings support the interesting possibility that n^* is a measure of the size of the cooperatively rearranging regions. Furthermore, our simulations show that SHD in water are qualitatively similar to those found in LJ systems, but the cluster shapes are strongly influenced by the geometry of the hydrogen bond network.

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