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What Do We Learn from the Local Geometry of Glass-Forming Liquids?

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We examine the local geometry of a simulated glass-forming polymer melt. Using the Voronoi construction, we find that the distributions of Voronoi volume $P(v_V)$ and asphericity $P(a)$ appear to be universal properties of dense liquids, supporting the use of packing approaches to understand liquid properties. We also calculate the average free volume $\langle v_f \rangle$ along a path of constant density and find that $\langle v_f \rangle$ extrapolates to zero at the same temperature T_0 that the extrapolated relaxation time diverges. We relate $\langle v_f \rangle$ to the Debye-Waller factor, which is measurable by neutron scattering.

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A fundamental mystery in the formation of glasses is the relationship of liquid structure to dynamics. While it has long been appreciated that many equilibrium and transport properties of dense fluids depend on the space available for molecular motion, the lack of methods to accurately compute or measure “free volume” and other measures of local structure have limited the development of this perspective for understanding fluid properties. Rahman [1] suggested that the Voronoi cells (where a cell is defined as the subvolume whose interior is closer to a specific atomic or molecular vertex than to any other vertex) may provide useful information about the local molecular environment. Furthermore, Voronoi volume v_V has been considered a possible measure of the local free volume that might be correlated with liquid relaxation [2,3], and there has been some tentative evidence to support this proposition [4,5]. Unfortunately, an unequivocal definition of free volume has been elusive, making it difficult to quantitatively test these ideas. However, for hard spheres, free volume can be rigorously defined and quantitatively related to the equation of state [6–8].

In this Letter, we focus on the local geometry of a simulated glass-forming polymer melt using a Voronoi analysis and a free volume approach based on a mapping to hard spheres. From the Voronoi approach, we find the striking result that the distribution of cell volumes $P(v_V)$ and the distribution of cell asphericities $P(a)$ are universal functions of temperature T and density ρ over a wide range of the liquid state, independent of the interaction potential. The existence of regularity in the structure of liquids is likely connected to the success of liquid state theories that focus on packing effects arising from core repulsion [9]. Utilizing a free volume definition related to hard spheres, we find that the extrapolated average free volume $\langle v_f \rangle$ appears to vanish at the same temperature T_0 where the extrapolated relaxation time τ of the coherent intermediate scattering function diverges. By relating $\langle v_f \rangle$ to the Debye-Waller (DW) factor $\langle u^2 \rangle$, we find that $\tau \sim \exp(\tilde{u}^2/\langle u^2 \rangle)$ (\tilde{u}

is a constant), as experimentally observed [10] and predicted by several models [11].

Our results are based primarily on molecular dynamics simulations of a melt containing 100 chains of “bead-spring” polymers, each chain consisting of 20 monomers. All monomers interact via a force-shifted Lennard-Jones (LJ) potential, truncated at 2.5σ , where σ is the LJ length parameter. Neighboring monomers along a chain also interact via a finitely extensible nonlinear elastic (FENE) spring potential. The FENE parameters— $k = 30\epsilon$ and $R_0 = 1.5\sigma$, where ϵ is the LJ energy parameter—are chosen to avoid crystallization. We present our results in reduced units [12]. The dynamics of this model (with only the potential shifted) was studied in Ref. [13]. Most of our simulations are in the range $0.35 < T < 4.0$ at constant density $\rho = 1.0$, and as a result the average Voronoi cell volume $\langle v_V \rangle = 1.0$ is constant. We also consider several additional densities to demonstrate the generality of our results. For reference, we fit τ to the power-law form $\tau \sim (T/T_{\text{MCT}} - 1)^{-\gamma}$ expected from mode coupling theory (MCT) [14] and estimate the crossover temperature $T_{\text{MCT}} = 0.35 \pm 0.01$.

Voronoi cell volume and asphericity.—The sensitivity of the Voronoi analysis to the local structure is particularly helpful for understanding changes along an isochoric cooling path, since the changes in local environment are more subtle than along an isobaric path. We implement an efficient algorithm for generating the Voronoi tessellation and the Delauney simplices [15]. From these calculations we first consider the statistical properties of the Voronoi cell volumes v_V . This leads to the striking result that the distribution of Voronoi cell volumes $P(v_V)$ appears to be universal, where the standard deviation $\sigma_v^2 \equiv \langle v_V^2 \rangle - \langle v_V \rangle^2$ decreases upon cooling (Fig. 1). The scaling of $P(v_V)$ suggests the existence of a single underlying geometrical structure of the system, and that system specifics, such as temperature, density, and interaction potential, are absorbed into the average and variance of the distribution.

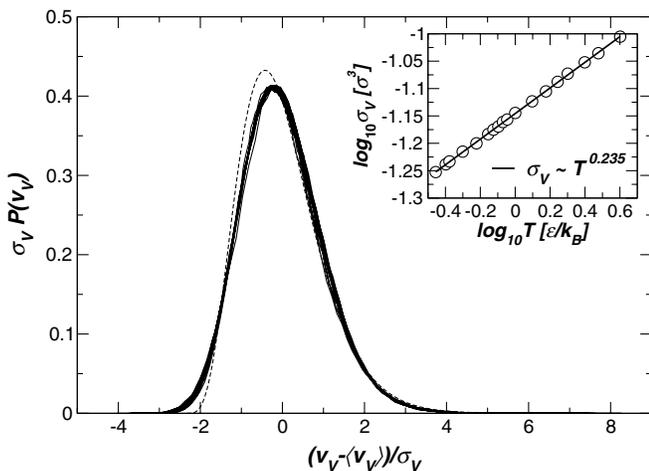


FIG. 1. Distribution of Voronoi cell volumes, shifted by the average Voronoi volume $\langle v_V \rangle$ and scaled by the root-mean-square deviation σ_v . The solid lines are data from 21 different state points of variable T and ρ (ranging from a very high T liquid to supercooled states), as well as data from seven state points of simulated liquid water, and one state point of simulated silicon. Most of the spread in the collapse is from the water data, for which we have inferior statistics. The dashed line indicates the ideal gas limit [16]. The inset shows the temperature dependence of σ_v along the $\rho = 1.0$ isochore.

To further test this possibility, we calculate $P(v_V)$ for $\rho = 0.9, 0.95, 1.05$, and 1.1 at $T = 1.0$ and find that $P(v_V)$ for different densities also scales to the same master curve. As an even more stringent test, we calculate $P(v_V)$ for configurations of simulated liquid water [17] and silicon; both liquids are anomalous due to the presence of directional bonding in the liquid state. We find that $P(v_V)$ for water and silicon collapses to the *same* universal curve as the polymer data, supporting the existence of a single underlying distribution of Voronoi volumes for dense liquids.

Such universal behavior suggests that a limit theorem [18] governs $P(v_V)$ for a wide range of possible interactions. The distribution is best fit by a log-normal distribution, but the deviations of the fit exceed the quality of the data collapse. This universal packing behavior likely explains why models based on short-range packing repulsion can successfully account for many liquid state properties [9]. This may serve as a point of departure for theoretical investigation of the origin of the scaling, which is beyond the scope of the present paper. The scaling must break down when particles are randomly distributed, as in the ideal gas limit. We find $P(v_V)$ for the liquid and ideal gas are similar, but differences occur at small v_V , where packing effects due to core repulsion in the liquid dominate (Fig. 1).

The scaling parameter σ_v follows a power law $\sigma_v \sim T^{0.23 \pm 0.01}$ (inset of Fig. 1). Since σ_v is the fluctuation in Voronoi volume, and compressibility κ_T is a measure of density fluctuations, it is tempting to relate the quantities [19]. However, σ_v measures volume fluctuations on the size scale of single particles, too small to expect a fluctua-

tion relation of the form $\kappa_T = \sigma_v^2 / (v_V k_B T)$ to hold [20]. On the other hand, σ_v should be related to the local restoring force of the fluid felt by a particle, since this controls the susceptibility of the fluid to local fluctuations. The restoring force is quantified by Ω_0 , the first nontrivial coefficient in an expansion of the velocity autocorrelation function [21]. Indeed, it has been found that Ω_0 scales approximately as $T^{1/4}$ [21], which we also confirmed for our system. This suggests a connection between σ_v and vibrational dynamics (given the uncertainties in the exponent values).

We further characterize local geometry by the asphericity a of the cells, which we quantify by the ratio of the radius of a sphere with the same volume as the cell to the distance between the Voronoi vertex and the nearest cell face. If the cell is spherical, the ratio is 1, while for any nonspherical cell, the ratio is greater than 1. On cooling, a decreases by $\approx 3\%$ over the range of our simulations, and thus Voronoi cells become slightly more spherical on average (inset of Fig. 2), as would be expected if the packing becomes more regular on cooling. The distribution of asphericities $P(a)$, like $P(v_V)$, also scales onto a single master curve using the same scaling method (Fig. 2). The width of the distribution, quantified by the standard deviation σ_a , monotonically decreases with decreasing T (not shown), also expected if packing becomes more regular on cooling. We find that σ_a follows a power law whose exponent changes slightly at $T \approx 1$, roughly the “onset” temperature for slow dynamics [22] and spatially heterogeneous dynamics [23]. However, the lack of corroborating evidence from the simulations of water and silicon suggests that the result for the polymer system is merely coincidental.

Free volume and dynamics.—We next focus our attention on possible connections between local structure and

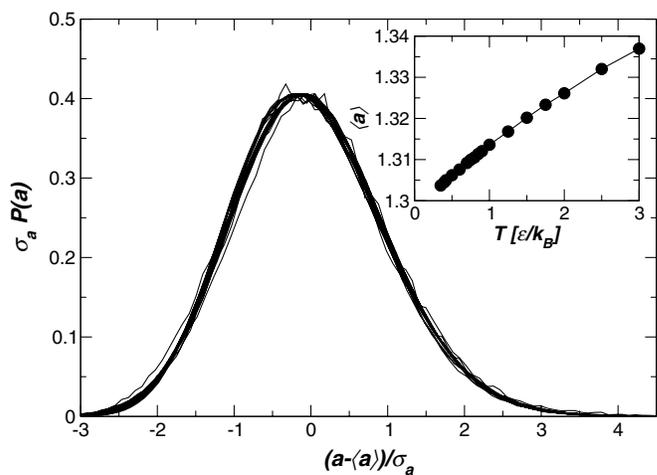


FIG. 2. Distribution of Voronoi cell asphericities, shifted by the average asphericity $\langle a \rangle$ and scaled by the root-mean-square deviation σ_a . The figure includes data from the same state points as Fig. 1. The inset shows the T dependence of $\langle a \rangle$ along the $\rho = 1.0$ isochore.

dynamics by examining the free volume. There have been numerous definitions of free volume [3,5,6], and thus it is not clear what the most appropriate and/or useful definition is. However, in the case of hard spheres, v_f of a particle can be unambiguously defined as the volume over which the center of a sphere can translate, given that all other spheres in the system are fixed (see, e.g., Fig. 1 of Ref. [24], where an algorithm for the calculation can also be found). This “rattle” free volume is rigorously related to the equation of state for hard spheres, as well as the void volume [8], and thus is an attractive definition.

In the case of soft-core repulsion, such a definition of v_f is not straightforward, since the average distance of closest approach depends on T . As done in Ref. [25] we define a T dependent effective hard sphere diameter, or Boltzmann diameter σ_B , by $U(r = \sigma_B) = E_c$, where U is the pair potential and E_c is the average kinetic energy of collision of an isolated pair of particles. Since E_c for this system is not known, we estimate $E_c = 2k_B T$, the exact result for hard spheres. We use only the nonbonded (Lennard-Jones) part of the potential to determine σ_B , since the bonding term has little effect on the distance of closest approach. On the other hand, the attractive part of the LJ interaction does contribute to σ_B and significantly affects the free volume and the overall dynamics [25]. By using the T dependent definition of σ_B , it is possible that $\langle v_f \rangle$ vanishes along paths of constant density, such as we study here, in contrast with free volume definitions tied to the macroscopic density.

We first consider the T dependence of the average free volume per monomer $\langle v_f \rangle$ and τ along the $\rho = 1.0$ isochore (Fig. 3). As expected, $\langle v_f \rangle$ decreases on cooling while τ increases. More significantly, we find that $\langle v_f \rangle$ may be well approximated by a power law $\langle v_f \rangle \sim (T/T_0 - 1)^\eta$, where $T_0 = 0.22 \pm 0.02$ and $\eta = 1.46 \pm 0.07$, if we allow both parameters to be free. For reasons that we will discuss, we expect $\eta = 3/2$, which results in a best fit value of $T_0 = 0.20$. We fit τ to the Vogel-Fulcher-Tammann (VFT) equation $\tau \sim \exp[A/(T - T_0)]$ and independently obtain an extrapolated divergence temperature $T_0 = 0.20$, which is typically slightly below the laboratory defined T_g . Hence, τ seems to diverge at the same T at which $\langle v_f \rangle$ extrapolates to zero, consistent with the possibility that the glass transition is related to the vanishing of the free volume, a central tenet of most free volume approaches [26]. By eliminating the T dependence from the expressions for $\langle v_f \rangle$ and τ , we obtain the parametric relation

$$\tau \sim \exp[(\tilde{v}/\langle v_f \rangle)^{2/3}], \quad (1)$$

where \tilde{v} is a constant. This relation is similar to but distinct from the Doolittle expression $\tau \sim \exp(v_0/v_f)$.

In order to explain the power-law dependence of $\langle v_f \rangle$ on T , and hence the unexpected relation between τ and $\langle v_f \rangle$, as well as provide an experimental connection, we must better understand the physical origin of $\langle v_f \rangle$. Since the free volume measures the space over which a particle can move

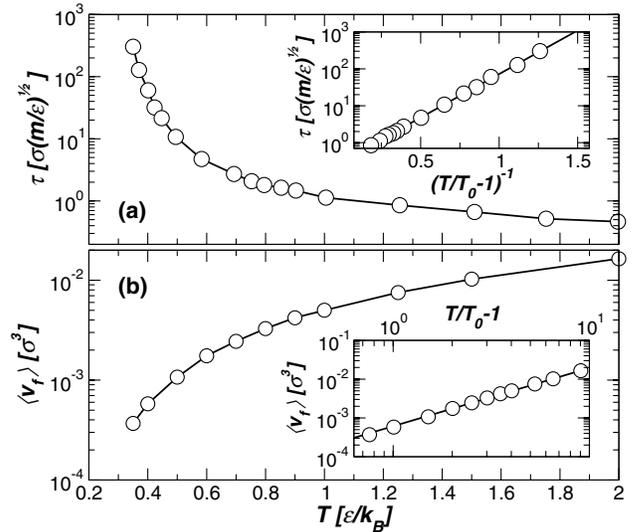


FIG. 3. (a) The relaxation time τ of the intermediate scattering function $F(q, t)$; we define τ at the time at which $F(q, t)$ has decayed by a factor of e^{-1} at the q value corresponding to the first maximum in $S(q)$. The inset shows the quality of the fit to the VFT form. (b) Average free volume per particle $\langle v_f \rangle$. The inset is a log-log plot to emphasize the power-law behavior.

before encountering the exclusion volume of neighboring particles (in the hard sphere mapping), it is natural to expect that free volume and the Debye-Waller factor, a measure of cage size, might be related. To test this, we define the DW factor $\langle u^2 \rangle \equiv \langle r^2(t = 1.022) \rangle$, where $t = 1.022$ is the approximate time of the crossover from ballistic to caged motion of the mean-squared displacement $\langle r^2(t) \rangle$. In Fig. 4 we make a parametric plot of $\langle v_f \rangle$ and $\langle u^2 \rangle^{3/2}$ and find a linear proportionality, supporting the hypothesis that free volume should be related to the DW factor. As a more stringent test, we consider the distributions $P(v_f)$ and $P(u^3)$, where $P(u^3)$ is calculated in the same fashion as the van Hove correlation function. The inset of Fig. 4 shows that both distributions are nearly exponential, but that stretching occurs at large volume. Exponential decay of $P(v_f)$ at large v_f is essential to recover the Doolittle relation in the Cohen-Turnbull formulation of free volume theory; since the Doolittle relation does not appear to hold for our data, the significance of the deviation from exponential decay is unclear. More importantly, the similarity of $P(v_f)$ and $P(u^3)$ for sufficiently large volume allows us to interpret v_f as a measure of the DW factor and apply ideas that have already been developed relating $\langle u^2 \rangle$ and bulk relaxation properties.

We substitute $\langle u^2 \rangle^{3/2}$ for $\langle v_f \rangle$ in Eq. (1) and obtain

$$\tau \sim \exp(\tilde{u}^2/\langle u^2 \rangle). \quad (2)$$

Several arguments have been put forth for this phenomenologically observed relation [10], based on the idea that the effective force constant localizing a particle is inversely proportional to $\langle u^2 \rangle$ and directly proportional to the energy barrier height [11]. The T dependence of $\langle u^2 \rangle$ is controlled

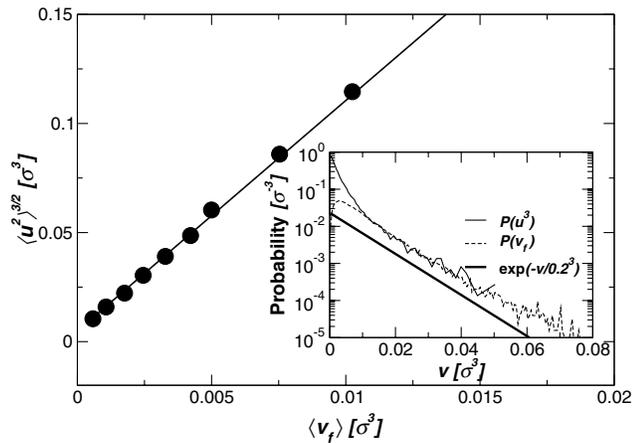


FIG. 4. Parametric plot of the Debye-Waller factor $\langle u^2 \rangle$ raised the 3/2 power (such that it has units of volume) as a function $\langle v_f \rangle$. The line indicates a least-square fit. The inset shows the distributions $P(u^3)$ and $P(v_f)$. The data for $P(u^3)$ are arbitrarily shifted to emphasize the similarity of the distributions. The bold line is an exponential $\exp(v/0.2^3)$, plotted as a guide to the eye.

by two factors: (i) inertial energy, resulting in a term proportional to $k_B T$, counterbalanced by (ii) a nearly T independent elastic energy proportional to $G_\infty \delta^3$, where G_∞ is the shear modulus and $\delta^3 \sim \mathcal{O}(v_f)$. This yields $\langle v_f \rangle \sim (T/T_0 - 1)^{3/2}$, where $T_0 \propto G_\infty \delta^3 / k_B$ since $\langle v_f \rangle \propto \langle u^2 \rangle^{3/2}$ [27]. Such a relationship is consistent with the VFT expression, as demonstrated by simple substitution. Additionally, the Adam-Gibbs expression $\tau \sim \exp(A/TS_{\text{conf}})$, successfully applied to a variety of model liquids [28], suggests a nontrivial relationship to the configurational entropy S_{conf} ; specifically, $TS_{\text{conf}} \propto \langle u^2 \rangle$ or $TS_{\text{conf}} \propto \langle v_f \rangle^{2/3}$. This offers an area of future consideration.

We have focused our attention on a limited subset of the predictions of free volume theories, which should be tested for a wider range of ρ and T . We tested, but did not find support for several additional hypotheses. Specifically, we also find that (i) free volume percolates at T well above T_g , and (ii) that no significant correlation exists between local volume of a specific monomer and its mobility. More details on these results will be provided in a future publication.

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