What do we learn from the local geometry of glass-forming liquids?

Francis W. Starr$^1$, Srikanth Sastry$^2$, Jack F. Douglas$^1$, and Sharon C. Glotzer$^{1,3}$

$^1$ Polymers Division and Center for Theoretical and Computational Materials Science, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
$^2$ Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bangalore 560064, INDIA and Departments of Chemical Engineering and Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA

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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 $P(v_f)$ 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.

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 has limited the development of this perspective for understanding fluid properties. Rahman\cite{1} suggested that the Voronoi cells (where a cell is defined as the sub-volume 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\cite{2,3}, and there has been some tentative evidence to support this proposition\cite{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\cite{6,7,8}.

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 $\rho$ over a wide range of the liquid state, independent of the interaction potential. While we are unable to quantitatively explain the origin of this universality, 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\cite{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 $\tau$ 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 $\tau \sim \exp(\hat{u}^2/\langle u^2 \rangle)$ ($\hat{u}$ is a constant), as experimentally observed\cite{10}, and predicted by several models\cite{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 potential, truncated at 2.5, in standard reduced units. Neighboring monomers along a chain also interact via a FENE spring potential. The FENE parameters are $k = 30$ and $R_0 = 1.5$, and are chosen to avoid crystallization. The dynamics of this model (with only the potential shifted) was studied in ref.\cite{12}. 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 $\tau$ to the power law form $\tau \sim (T/T_{MCT} - 1)^{-\gamma}$ expected from mode coupling theory (MCT)\cite{13}, and estimate the crossover temperature $T_{MCT} = 0.35 \pm 0.01$, where the uncertainty represents the range of $T$ for which a power law fits well to the data.

A. Voronoi Cell Volume and Asphericity

The sensitivity of the Voronoi analysis to 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 tessalation and the Delauney simplices\cite{14}. 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. To further test this possibility, we calculate $P(v_V)$ for $\rho = 0.9, 0.95, 1.05$, and...
con collapses to the same distributed in the ideal gas limit. Point out that scaling must break down at sufficiently low which is beyond the scope of the present paper. We also repulsion can successfully account for many liquid state likely explains why models based on short-range packing distribution, but the deviations of the fit exceed the qual-

ity of the data collapse. This universal packing behavior also 

rem \[16\] governs distribution of Voronoi volumes for dense liquids.

Such universal behavior suggests that a limit theorem \[14\] 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 \[3\]. 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. We also point out that scaling must break down at sufficiently low density or high temperature, since particles are randomly distributed in the ideal gas limit.

The scaling parameter \(\sigma_v\) follows a power law \(\sigma_v \sim T^{0.23\pm0.01}\) (inset of Fig. 1). Since \(\sigma_v\) is the fluctuation in Voronoi volume, and compressibility \(\kappa_T\) is a measure of density fluctuations, it is tempting to relate the quantities \[17\]. However, \(\sigma_v\) measures volume fluctuations the size scale of single particles, too small to expect a fluctuation relation of the form \(\kappa_T = \sigma_v^2/(v_V k_B T)\) to hold \[18\]. On the other hand, \(\sigma_v\) 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 \(\Omega_0\), the first non-trivial coefficient in an expansion of the velocity auto-correlation function \[14\]. Indeed, it has been found that \(\Omega_0\) scales approximately as \(T^{1/4}\) \[19\], which we also confirmed for our system. This suggests a connection between \(\sigma_v\) and vibrational dynamics (given the uncertainties in the exponent values). At fixed \(T = 1\), we further observe \(\sigma_v \sim \rho^{-3.4}\) over the narrow range \(0.9 < \rho < 1.1\). In the cases of simulated water and silicon, our data is not able to confirm or exclude power-law scaling of \(\sigma_v\).

We further characterize local geometry by the asphericity \(a\) of the cells, which we define 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 one, while for any non-spherical cell, the ratio is greater than one. 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 \(\sigma_a\), monotonically decreases with decreasing \(T\) (not shown), also expected if packing becomes more regular on cooling. We find that \(\sigma_a\) follows a power law whose exponent changes slightly at \(T \approx 1\), roughly the “onset” temperature for slow dynamics \[20\] and spatially heterogeneous monomer motion \[21\]. However, the lack of corroborating evidence from the simu-

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**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 \(\sigma_v\). The figure includes data from 21 different state points of variable \(T\) and \(\rho\) (ranging from a very high \(T\) liquid to supercooled states), as well as data from 7 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 inset shows the temperature dependence of \(\sigma_v\) along the \(\rho = 1.0\) isochore.

**FIG. 2:** Distribution of Voronoi cell asphericities, shifted by the average asphericity \(\langle a \rangle\) and scaled by the root-mean-square deviation \(\sigma_a\). 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.
lations of water and silicon suggests that the result for the polymer system is merely coincidental. Similar calculations for other simple and molecular liquids will be useful to identify the common features of cell geometry in liquids.

B. Free Volume and Dynamics

We next focus our attention on possible connections between local structure and 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. \([22]\), 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 \([3]\), 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. \([23]\) we define a \(T\) dependent effective hard sphere diameter, or Boltzmann diameter \(\sigma_B\), by \(U(\sigma = \sigma_B) = E_c\), 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 \(E_c = 2k_BT\), the exact result for hard spheres. Additionally, we use only the non-bonded (Lennard-Jones) part of the potential to determine \(\sigma_B\), since the bonding term has little effect on the distance of closest approach. By using the \(T\) dependent definition of \(\sigma_B\), 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 \(\tau\) (Fig. 3). As expected, \(\langle v_f \rangle\) decreases on cooling while \(\tau\) 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 \(T_0 = 0.20\) and \(\eta = 1.46\), 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 \(\tau\) to the Vogel-Fulcher-Tamman (VFT) equation \(\tau \sim \exp[A/(T - T_0)]\) and independently obtain an extrapolated divergence temperature \(T_0\), which is typically slightly below the laboratory defined \(T_g\). Hence, \(\tau\) 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 vanishing of free volume, a central tenet of most free volume approaches \([24]\). By eliminating the \(T\) dependence from the expressions for \(\langle v_f \rangle\) and \(\tau\), we obtain the parametric relation

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

where \(\tilde{v}\) is a constant. This relation is similar to, but distinct from the Doolittle expression \(\tau \sim \exp(v_0/v_f)\), later rationalized by the Cohen-Turnbull models that assume an exponential distribution of free volume \([2]\).

In order to explain the power-law dependence of \(\langle v_f \rangle\) on \(T\), and hence the unexpected relation between \(\tau\) 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 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 exponen-
We also find that (i) free volume percolates at a well defined volume — become important. However the extrapolation of the 3/2 power (such as in units of volume) as a function of \(v_f\). The line indicates a least-square fit. The inset shows the distributions \(P(\langle u \rangle)\) and \(P(v_f)\). The data for \(P(\langle u \rangle)\) is arbitrarily shifted to emphasize the similarity of the distributions. The bold line in an exponential \(\exp(v/2^{3})\), plotted as a guide to the eye.

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 \(\langle u \rangle^{2}\) and directly proportional to the energy barrier height \([11]\). The \(T\) dependence of \(\langle u \rangle^{2}\) is controlled by two factors: (i) inertial energy, resulting in a term proportional to \(k_BT\), counterbalanced by (ii) a nearly \(T\) independent elastic energy proportional to \(G_{\infty}\), the shear modulus and \(\delta^{3} \approx \mathcal{O}(\nu v)\). This immediately yields \(\langle v_f \rangle \sim (T/T_0 - 1)^{3/2}\), where \(T_0 \propto G_{\infty}\delta^{3}/k_B\), since \(\langle v_f \rangle \propto \langle u \rangle^{3/2}\). Such a relationship is consistent with the VFT expression, as demonstrated by simple substitution. Additionally, the Adam-Gibbs expression \(\tau \sim \exp(A/T S_{\text{conf}})\), successfully applied to a variety of model liquids \([12]\), suggests a non-trivial relationship to the configurational entropy \(S_{\text{conf}}\); specifically, \(T S_{\text{conf}} \propto \langle u \rangle^2\) or \(T S_{\text{conf}} \propto \langle v_f \rangle^{2/3}\). This offers an area of future consideration.

We have focused our attention on a limited subset of the predictions of free volume theories. We 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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FIG. 4: Parametric plot of the Debye-Waller factor \(\langle u \rangle^{3/2}\) raised the the 3/2 power (such that has units of volume) as a function of \(v_f\). The line indicates a least-square fit. The inset shows the distributions \(P(\langle u \rangle)\) and \(P(v_f)\). The data for \(P(\langle u \rangle)\) is arbitrarily shifted to emphasize the similarity of the distributions.