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Putative role of attractive and repulsive forces in the glass transition

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At a given temperature a balance between repulsive and attractive molecular forces determines liquid density. As temperature is lowered, attractive forces increase, but eventually saturate and asymptote to a near fixed value. At saturation, the attractive/repulsive force balance stabilizes the liquid density, which thereafter becomes effectively temperature independent. Configurational entropy also saturates, but at a much lower temperature. Once entropy begins to saturate, it converges to zero at absolute zero. There is no second order phase transition nor is there a divergent temperature above absolute zero predicted for glass relaxation phenomena. Using a phenomenological argument, it is shown that the relaxation time for volume relaxation varies inversely with configurational entropy. Stoichiometric electron density is proposed as a metric for repulsive force strength, which was determined at T_g and averaged 0.61±0.03 mol/cc for 15 polymers that contain oxygen and 0.53±0.02 mol/cc for 7 hydrocarbon polymers. Qualitatively, similar polymer liquids that pack to higher electron densities at a given temperature are expected to experience a glass transition earlier as temperature is lowered. For certain polymer types, the glass transition appears to be an isoelectronic state.

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1. Introduction

Ever since the seminal work of Gibbs and DiMarzio (GD) [1], it has been understood that repulsive forces appear to dominate the glass transition and glass structure. The basic GD premise is the number of ways molecules can randomly pack into a disordered structure, which determines its configurational entropy, reaches a limiting value as the glass transition is approached [1–5]. A hard sphere fluid exemplifies this physical principle, as it appears to undergo a glass transition at the Kauzmann density at a volume fraction of 0.545 [6].

However, as is well known, the experimental glass transition is a kinetic phenomenon that may occur well before this ideal "packing limit" obtains. This observation motivated Adams and Gibbs [2] to link GD thermodynamics to glass kinetics over 50 years ago. Their basic idea was the reduction in configurational entropy increases the size scale for cooperative molecular motion as the glass transition is approached, which slows down structural rearrangements. This approach is still widely invoked today to describe glass transformation kinetics [7–10].

In a previous publication [11], it was suggested that the glass transition might also be a manifestation of an "energy saturation" mechanism. At a given temperature above the glass temperature and fixed pressure, a balance between repulsive and attractive forces determines liquid density. Since the strength of attractive interactions initially scale as $1/T$, decreases in temperature increase density. However, if attractive interactions are short-ranged, attractive forces must eventually saturate at high densities.

Two important properties of the energy saturation model developed herein will be advanced: Above the glass transition temperature, liquid density is controlled by the equation of state and varies linearly with temperature. When cooled, this linear temperature behavior begins to breakdown, which is one signature of a liquid-to-glass transition. Our primary thesis is that this departure, which is cooling rate dependent, manifests configurational energy saturation. Once configurational energy begins to saturate, the equilibrium density begins to asymptote to a limiting value. Even if cooled infinitely slowly to maintain equilibrium, this density departure from its linear temperature trajectory is expected. However, the observed kinetics, embodied in the ability of the equilibrium density to keep up with a given cooling rate, should be controlled by the *temperature gradient on the chemical potential*. For example, after a rapid temperature quench of δT, a liquid is in a non-equilibrium state with its volume V displaced from its equilibrium value of V_{eq}. The thermodynamic driving force for volume recovery $(V \rightarrow V_{eq})$ will be governed by the magnitude of the

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corresponding chemical potential displacement (displaced from its equilibrium value μ_{eq} at the quench temperature):

$$\delta\mu = \left(\frac{\partial\mu}{\partial T}\right)_P \delta T = -S\,\delta T \tag{1}$$

The corresponding relaxation time (τ) for volume recovery for a temperature quench or jump will vary as

$$\tau \sim \frac{1}{|\delta\mu|} \sim \frac{1}{S} \tag{2}$$

Volume relaxation requires configurational rearrangements so the inverse dependence of the relaxation time on entropy, especially the configurational contribution to the entropy, becomes rate controlling. During an isothermal volume contraction, the thermal entropy remains fixed and only the configurational entropy (the principle driving force) changes.

The cause and effect relationships are as follows: although mediated by kinetics, the underlying root cause for the breakdown of the linear density-temperature relationship is configurational energy saturation as reflected in the equation of state. The ability of liquid density to keep up with the cooling rate is governed by liquid configurational entropy. Even after configurational energy saturates, configurational entropy has not. At energy saturation multiple configurations yield the same saturation energy. The temperature where entropy begins to saturate (99% level) is well below where energy begins to saturate at the 99% level.

The above phenomenological argument that glass transition kinetics are controlled by entropy is superficially compatible with the microscopic theory of Adam and Gibbs [2]. However, a number of important differences exist between the AG kinetic adaption of the Gibbs-DiMarzio model [1] and the QC chain model. With regards to the latter: (1) There is no second order phase transition underlying the glass transition. (2) There is no divergent temperature above absolute zero predicted for glass relaxation phenomena; the implication is that the temperature singularity at T_∞ in the empirical VFT relaxation equation is apparent, not real:

$$\tau(T) = \tau_0 \exp\left(\frac{B}{T - T_\infty}\right) \tag{3}$$

(3) The underlying cause for why density departs from temperature linearity as the glass transition is approached differs. Configurational energy saturation is not a property of the GD model nor is it a property belonging to any model that uses a mean-field interaction energy (van der Waals). (4) The essential hypothesis of the AG model is that the reduction in configurational entropy increases the size scale for cooperative molecular motion as the glass transition is approached. The general thermodynamic approach expressed above does not appeal to any specific molecular mechanism. *In the quench scenario, the dynamics of equilibration can be regarded as a random thermal rearrangement of structure biased by attractive interactions that favor configurations of higher density and lower entropy.*

Point (1) above is one that others have emphasized. It seems quite possible that the entropy may just “bend over” and approach a limiting value at absolute zero [12–14]. This is just what the energy saturation model predicts. The excess configurational entropy varies nearly linearly with temperature before it begins to saturate and then “turns abruptly” and converges to zero at zero temperature. Extrapolation of the linear behavior to zero temperature defines an apparent non-zero Kauzmann temperature, T_K with the implication that $T_\infty = T_K$. The absence of a true divergent temperature has also received support from others [15–17].

In our previous publication [11], thermodynamics of energy saturation were demonstrated for a square well (SW) fluid with energetics treated in a quasi-chemical (QC) approximation. In contrast, a mean-field treatment of this model does not yield energy saturation. In the present study, this model is extended to polymers *via* a tangent hard sphere (HS) chain where each monomer interacts with other monomers through a SW potential. A SW potential has the form:

$$\phi(R) = \begin{cases} \infty & : R < \sigma \\ -\varepsilon & : \sigma \le R \le \lambda\sigma \\ 0 & : R > \lambda\sigma \end{cases} \tag{4}$$

where σ is the HS monomer diameter, and λ scales the range of the attractive interaction of strength $-\varepsilon$ Monomer-monomer energetics are treated in a QC approximation illustrated in Fig. 1.

The structure of the paper is as follows: Sections 2-3 describe the QC tangent HS chain model and its thermodynamic properties, especially energy and entropy saturation. The 4th Section describes the differences in mean-field and QC energetics relevant to the concept of energy saturation, which is followed by Section 5 that looks at the thermodynamic evidence for an ideal glass state. Section 6 examines the excess entropy behavior of the model and Section 7 explores how repulsive forces and electron density are related.

2. Quasi-chemical approximation

Consider a tangent sphere chain of r HS monomers (*aka* r-mer chain) attractively interacting with other monomers through a SW potential (see Fig. 1). The maximum possible interaction energy per chain is $-rn_{\max}\varepsilon$ and may involve both intermolecular and intramolecular monomer-monomer interactions. In a QC approximation, the probability P_n that n spheres are within the attraction

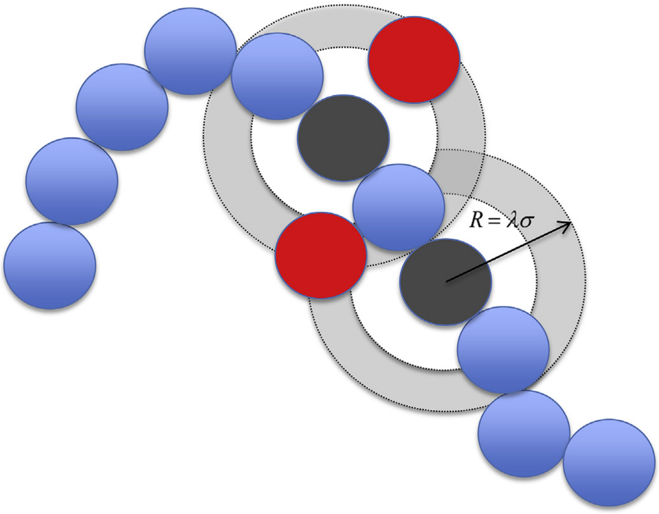

Fig. 1. Two-dimensional schematic of a tangent sphere chain illustrates the attractive domains (gray annuli) of the 2 black spheres. These attractive shells have a volume of $8(\lambda^3 - 1)v_0$ where $v_0 = (\pi/6)\sigma^3$ is the HS volume. As illustrated, $\lambda = 3/2$ and yields an attractive domain volume of $19v_0$. The white annuli around the 2 black spheres with volumes $8v_0$ are the excluded volume regions where no other sphere center may enter. The red sphere centers are in the attractive domains of the 2 black spheres and one red sphere is in both domains. These red spheres might belong to other chains or to the same chain, but the 2 blue spheres directly connected to the black spheres do not contribute to the attractive interaction. The maximum number of spheres that can be accommodated in an attractive domain is set at 10. When the 2 nearest-neighbor connected spheres are added, the maximum packing density ($\eta_{\max}$) around any sphere equals $12/19 = 0.632$, which corresponds to the random close-packing value for hard spheres [18,19].

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