

Significance of the free volume for metastability, spinodals, and the glassy state: An exact calculation in polymers

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A lattice model of semiflexible linear chains (with equilibrium polydispersity) containing free volume is solved exactly on a Husimi cactus. A metastable liquid (ML) is discovered to exist only at low temperatures and is distinct (and may be disjoint) from the supercooled liquid (SCL) that exists only at high temperatures. The free volume plays a significant role in that the spinodals of the ML and SCL merge and then disappear as the free volume is reduced. The Kauzmann temperature T_K occurs in the ML without any singularity. At $T_{MC} > T_K$, the ML specific heat has a peak. For infinitely long polymers, the peak height diverges and the free volume vanishes at T_{MC} , resulting in a continuous liquid-liquid transition. Contrary to the conventional wisdom, both T_K and T_{MC} occur in the ML and not in the SCL.

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The thermodynamic and kinetic aspects of the liquid-glass transition at T_G provide an interesting duality, which presents one of the most challenging problems in theoretical physics [1–11]. It is fair to say that there yet exists no completely satisfying theory of the glass transition even though some major progress has been made recently [6–11]. The most successful theory that attempts to describe *both* aspects with some respectable success is based on the “free-volume” model of Cohen and Turnbull [3]. The concept of free volume has been an intriguing one that pervades physics but its consequences and relevance are not well understood [12], at least in our opinion. In this theory, the glass transition (GT) occurs when the free volume becomes sufficiently small to impede the mobility of the molecules [13]. The time dependence of the free-volume redistribution, determined by the energy barriers encountered during redistribution, provides a kinetic view of the transition, and must be properly accounted for. This approach is yet to be completed satisfactorily. The thermodynamic view treats the ideal glass transition as a continuous transition in the metastable state, especially in polymers [1,2,4(a)]. In polymers, one must make a distinction between the interaction strengths of the end group and the middle group with the free volume, in addition to their mutual interaction [14]. We have used these interactions [12(b)] to explain some unexpected experimental results on the variation of T_G with molecular weight [15], by studying a completely flexible polymer lattice model. There was no crystal (CR) phase and, hence, metastability. Thus, the GT itself was not investigated. We will now introduce semiflexibility following [11] to study the GT, the metastability and spinodals, and the role of free volume and entropy.

It is commonly believed that the lack of free volume and the entropy crisis are at least two important factors that control the glassy state, and that they are interrelated. However, the entropy crisis can exist even in an incompressible system [11] (no free volume). Furthermore, thermodynamics requires the entropy but not the volume or the free volume to drop as the temperature is reduced. Thus, there is serious doubt about the significance of the free volume for the glass, which is the central issue to be investigated.

In the mode-coupling (MC) theory [7], the ergodicity is lost completely, and structural arrest occurs at a temperature T_{MC} , which lies well above the customary glass transition temperature T_G . Consequently, the correlation time and the viscosity diverge due to the caging effect. The diverging viscosity can be related to the vanishing free volume [3(a),13], which might suggest that *the MC transition is the same as the glass transition*. This does not seem to be the consensus at present. Thus, it is not clear if the free volume is crucial for the MC transition or the GT, and this needs to be clarified.

It is quite remarkable that a supercooled liquid (SCL) usually does not end in a spinodal. However, some fluids that contain hydrogen bonding, like water, are exceptions [16]. Their unusual behavior is thought to be related to their negative expansion coefficient. However, the implications of the SCL spinodal for the GT are not well understood, and need to be investigated. One must also investigate why SCL spinodals do not seem to occur in systems without hydrogen bonding.

In classical statistical mechanics, the kinetic energy contribution to the partition function can be factored out to leave behind the configurational partition function. The entropy contribution $S_{KE}(T)$ from kinetic energy is independent of the configuration; hence, it is the same for a CR and a SCL. It merely plays the role of an additive constant so that we need to consider only the configurational entropy for studying metastability. The latter appears in the configurational partition function and cannot be *negative* if the corresponding state is to occur in nature [17]. One usually approximates it by $S_{ex}(T) \equiv S_{SCL}(T) - S_{CR}(T)$, the excess SCL entropy over that of the CR. This requires assuming that $S_{CR}(T) = S_{KE}(T)$, which is not generally true. The SCL specific heat $C_{SCL}(T)$ is much higher than the CR specific heat $C_{CR}(T)$ [1,2]. Hence, the drop in $S_{SCL}(T)$ is much stronger than in $S_{CR}(T)$ as T falls, so that the “extrapolated” $S_{SCL}(T)$ becomes less than $S_{CR}(T)$ at low enough temperatures below T_G , which according to Kauzmann [1] presents a catastrophe that has to be avoided by some transition. However, as

shown recently for an incompressible and infinitely long polymer chain system [11], one can have $S_{\text{ex}}(T) < 0$ without violating thermodynamics. Indeed, there are real systems like ^4He for which the entropy of the equilibrium liquid (EL) can be less than its crystal entropy $S_{\text{CR}}(T)$. The signature of the Kauzmann paradox is taken there [11] not as a negative S_{ex} , but as the *entropy crisis* caused by the configurational entropy becoming negative [17]. In any lattice model, like the one considered in Ref. [11] and here, $S_{\text{KE}}(T) = 0$; hence, the entropy is only configurational. The entropy $S_{\text{SCL}}(T)$ remains positive, but the entropy $S_{\text{ML}}(T)$ of the metastable liquid (ML) vanishes and becomes negative below some nonzero lower temperature T_K . The latter is impossible as noted above and signals the Kauzmann catastrophe [11]. The entropy crisis occurs in the ML and not in the SCL, neither of which exhibits any spinodal [11]. The observed continuous liquid-liquid (L-L) transition at T_{MC} between the SCL and the ML is conjectured to be the thermodynamic transition underlying the dynamic MC transition.

Do these results survive in the presence of free volume? How does finite polymer size affect these conclusions? Are there spinodals associated with the SCL or the ML? What is their significance? What is the physics behind the SCL-ML transition? Will it disappear in the presence of free volume? What distinguishes T_K and T_{MC} ? Does the free volume vanish at a nonzero temperature? We attempt to answer these questions below.

Model. One usually considers a square lattice, in which there are $2N$ lattice bonds provided we neglect surface corrections. Let N_p , N_g , N_h , N_M , N_v , $B \equiv N_m - p$, and p denote the total number of pairs of parallel bonds, gauche bonds, hairpin turns, middle groups (M), voids (v), chemical bonds, and polymers, respectively. Here $N_m \equiv N - N_v$ is the number of monomers. (For the Hamilton walk limit studied in Ref. [11], $p = 1$.) There is a three-site bending penalty $\varepsilon > 0$ for each of the two possible gauche (g) bonds with respect to a polymer bond. There is no penalty for a trans bond. There is a four-site interaction energy $\varepsilon' > 0$ for each pair of neighboring parallel bonds. The third energy of interaction is ε'' for each hairpin turn. The configurational interaction energy is given by $\mathcal{E} = \varepsilon N_g + \varepsilon' N_p + \varepsilon'' N_h = \varepsilon(N_g + aN_p + bN_h)$, where $a = \varepsilon'/\varepsilon$ and $b = \varepsilon''/\varepsilon$. We introduce $w = \exp(-\beta\varepsilon)$, $\beta = 1/T$, $w' = w^a$, and $w'' = w^b$, and replace T/ε by T , so that the temperature is measured in the units of ε . We introduce the middle group activity η_M , and the end-point activity H . Let the exchange energies between different pairs of species, middle group, end group (E), and voids, be ε_{ME} , ε_{Mv} , and ε_{Ev} , and the corresponding Boltzmann weights be w_{ME} , w_{Mv} , and w_{Ev} , where $w_{ij} = \exp(-\beta\varepsilon_{ij})$, $i \neq j$, $i, j = v, M$, or E . Let N_{ij} denote the nearest-neighbor contacts between dissimilar species i and j . The grand canonical partition function is

$$Z_N = \sum \eta_M^{N_M} H^{2p} w^{N_g} w'^{N_p} w''^{N_h} \prod_{ij} w_{ij}^{N_{ij}}. \quad (1)$$

The sum is over distinct values of N_M , N_g , N_p , N_h , N_{ij} , and p for a given value of N . The corresponding free energy [18] gives the pressure Pv_0 ; here, v_0 represents the lattice

cell volume; we henceforth set $v_0 = 1$. For $\eta_M \rightarrow \infty$, we retrieve the Hamilton walk limit studied earlier [11].

The general model is capable of describing vaporization, melting, and sublimation. In addition, it also describes the liquid-liquid transition. The P - T plane calculation in the grand canonical ensemble is carried out at constant chemical potentials. Depending on how we cross the vaporization curve in the P - T plane, we can obtain supercooled or superheated liquid or vapor. This should not be a surprise. The same will happen across other transition curves. We need to make the following two important observations.

(1) One of the configurations in Z_N represents the vacuum in which all sites are covered by voids, and it contributes 1 to Z_N . The remaining terms are all non-negative. Hence, P must be non-negative in equilibrium. Moreover, it must be a maximum in the equilibrium state. However, there is no reason to expect P to be non-negative in metastable or supercooled or superheated states. Indeed, it is easy to find such states with negative pressures. For example, if the vacuum is not allowed for some metastable states, then Z_N need not to be larger than 1. In that case, the pressure could be negative. Despite this, the specific heat or other thermodynamic stability requirement must be obeyed for these nonequilibrium states [17]. Consequently, we never obtain unstable states in an exact calculation like the one we carry out in this work. Because of this, the termination of any state in the interior of the parameter space will correspond to its spinodal limit. As usual, the signature of the spinodal will be a diverging susceptibility like the specific heat. The termination of a state at the boundary of the parameter space gives a Nernst point, where some susceptibilities vanish [19]. Nernst points should not be confused with spinodals.

For the equilibrium state, P must diverge as the free volume vanishes. However, this need not be the case for non-equilibrium states. Indeed, we will see that P will invariably remain finite in such states even when the free volume vanishes.

(2) The current polydisperse model has an extra activity H because of which we have a fluctuating degree of polymerization (DP) compared to the monodisperse model containing polymers of a fixed DP. Let \bar{M} denote the DP. Setting $N_m = (\bar{M} - 2)p$ in Eq. (1), we see that $\eta_p = \eta_M^{\bar{M}-2} H^2$ represents the activity for a polymer chain of DP \bar{M} . Keeping η_p fixed will allow us to use the current model to draw quantitative conclusions about the corresponding monodisperse model containing chains of DP \bar{M} .

Recursive lattice solution. The above model, which cannot be solved exactly on a square lattice, is solved exactly on a square Husimi cactus; see Ref. [11] for details. The exactness of the solution ensures that thermodynamics is never violated. The solution forms an approximate theory on a square lattice. The cactus levels are indexed sequentially as we move outward away from the center ($m=0$) of the cactus, so that the four vertices in a square are indexed m for the bottom vertex, $m+1$ for the two intermediate vertices, and $m+2$ for the top vertex. There are three additional states of a vertex of the cactus in addition to the four previous states ($\alpha = I, O, R$, and L) defined in Ref. [11]. Two of the new

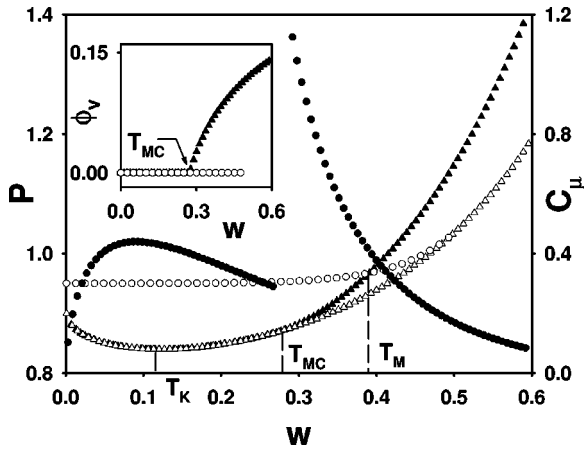


FIG. 1. The equation of state for the EL or SCL (\blacktriangle), ML (\triangle), and CR (\circ); use the left hand axis. We consider $a=0.1$, $b=0$, $c_{MV}=0.07$, $\mu_M=1$. The specific heat C_μ (\bullet) for the EL and SCL; use the right hand axis. The inset shows the free volume density in the CR (\circ) and EL or SCL (\blacktriangle). On the w scale we show $T_M=0.391$, $T_{MC}=0.273$, and $T_K=0.124$.

states at a vertex correspond to having an end point attached to a polymer bond that (i) lies above the vertex, and (ii) lies below the vertex. The remaining new state corresponds to having a void. It is convenient to introduce normalized energies $c_{ij} \equiv \varepsilon_{ij}/\varepsilon$, so that $w_{ij} \equiv w^{c_{ij}}$, and normalized chemical potentials μ_E, μ_M via $H \equiv w^{-\mu_E}$ and $\eta_M \equiv w^{-\mu_M}$.

We introduce seven partial partition functions $Z_m(\alpha)$ corresponding to the seven states at each cactus level, indexed by m . We then construct the recursion relations among these partial partition functions at successive levels that can be written symbolically as $Z_m(\alpha) \equiv J_\alpha[\{Z_{m+1}(\alpha')\}, \{Z_{m+2}(\alpha'')\}]$, where J_α is a cubic polynomial [quadratic in $Z_{m+1}(\alpha')$ and linear in $Z_{m+2}(\alpha'')$]. The nature of the fix-point (FP) solution determines the bulk behavior. To study the FP solution, we introduce seven ratios $x_m(\alpha) \equiv Z_m(\alpha)/[Z_m(L)+Z_m(R)]$, $x_m(L)+x_m(R)=1$. We consider the one-cycle and two-cycle FP solutions describing the disordered and crystal phases in the model [11]. In the one-cycle solution, the ratios are the same at each successive level, given by $x(\alpha)$. In the two-cycle solution, they alternate between $x(\alpha)$ and $x'(\alpha)$ from one level to another. The FP solutions are obtained numerically, and we present the results below. The complete recursion relations are given elsewhere [20]. The calculations are done at fixed μ_E , μ_M , and c_{ij} as a function of T .

Infinite polymers ($H=0$). We show the P - T equation of state for the EL or SCL (\blacktriangle), ML (\triangle) and CR (\circ) in Fig. 1; use the left axis. The equilibrium phase has the maximum pressure, so that the EL and CR are the stable phases above and below the melting temperature T_M . The EL turns into a SCL below T_M and disappears at T_{MC} , below which the ML becomes the only possible metastable state. The specific heat C_μ (\bullet) at constant chemical potentials for the EL or ML (use the right axis) shows a divergence at T_{MC} due to a continuous transition. In the inset, we show the free-volume density ϕ_v as a function of T for the EL or SCL (\blacktriangle) and the CR (\circ). We are immediately struck by its disappearance in a

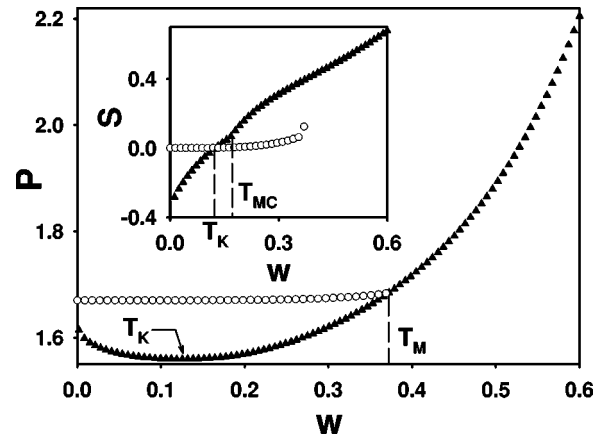


FIG. 2. The equation of state for finite polymers with free volume for the CR (\circ) and EL or SCL (\blacktriangle). We consider $a=0.66$, $c_{MV}=0.3$, $c_{ME}=0.01$, $c_{EV}=0.1$, $\mu_M=2$, $\mu_E=-6$, and $b=0$. On the w scale we show $T_M=0.372$, $T_{MC}=0.166$, $T_K=0.124$. The inset shows the entropy per site for the CR (\circ) and EL or SCL (\blacktriangle)

singular manner at T_{MC} . The free volume is identically zero in the CR and ML (not shown). Since the entropy S per unit volume is the derivative $(\partial P/\partial T)_\mu$ at fixed chemical potentials, we conclude that the entropy in the ML vanishes at T_K ($<T_{MC}$), the Kauzmann temperature, and becomes negative below it. Thus, the ML is a physical state only at and above T_K , even though C_μ is positive everywhere.

Finite polymers ($H>0$). The singularity in the equation of state at T_{MC} disappears (Fig. 2) for nonzero H . This makes the EL or SCL and the ML the same phase (\blacktriangle), which continues all the way down to T_K , where it terminates because of the *entropy crisis*. We also show the CR (\circ) equation of state. However, the free volume still falls rapidly in the vicinity of T_{MC} to an extremely small value and goes to an even smaller and nonzero value at T_K . The free volume in the CR also remains extremely small. The entropy for the EL or SCL (\blacktriangle) and CR (\circ) is shown in the inset.

In Fig. 3, we show the vapor phase ($\triangle, \blacktriangle, \square$), the CR (\diamond, \bullet, \circ), and the liquid phases EL, ML, and SCL ($\blacksquare, \blacktriangledown$) for $\mu_M=0.25, 0.38$, and 0.4 ; the specific heat C_μ for the ML and SCL is shown in the inset. For $\mu_M=0.25$, the SCL (\blacksquare) terminates into its spinodal below T_v , the temperature below which the vapor phase (\triangle), whose pressure is slightly larger than zero, becomes stable. The CR phase (\diamond), which starts at absolute zero, has negative pressure and ends in a spinodal. There is a *third* disordered phase (ML, \blacksquare), which originates at absolute zero and exists only near $T=0$, and has the lowest possible (negative) pressure. It is disjoint from the SCL and is unphysical as it has negative entropy over its entire range. In addition, its specific heat (\bullet) (see the inset) also does not diverge where it ends; thus, its end is not a spinodal. The specific heat (\bullet) of the SCL, on the other hand, diverges at its spinodal. The ML phase becomes physically relevant only where it has non-negative entropy (solid curve, \blacktriangledown). For $\mu_M=0.38$, the ML and SL (solid curve) are still disjoint, and each terminates in a spinodal, where C_μ (dashed curve in the inset) diverges. What is

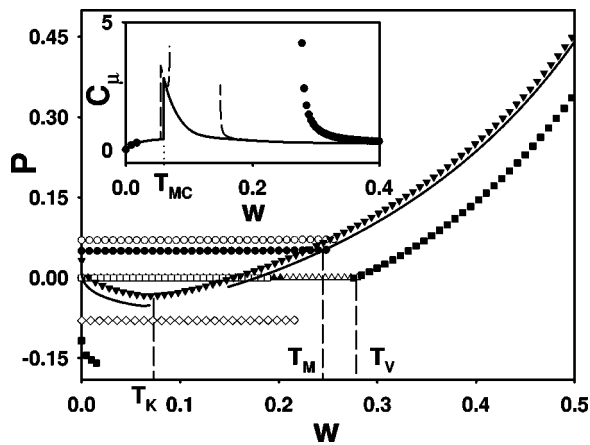


FIG. 3. Evolution of the mode-coupling transition with increasing μ_M . We show the equation of state for the vapor phase ($\triangle, \blacktriangle, \square$), the CR (\diamond, \bullet, \circ), and various branches of the liquid (\blacksquare , solid curve, \blacktriangledown) for $\mu_M=0.25, 0.38$, and 0.4 , respectively. The rest of the parameters are the same as in Fig. 2. The vaporization temperature of the liquid-vapor transition is also shown. In the inset we show the specific heat of the liquid state for $\mu_M=0.25$ (\bullet), 0.38 (dashed line), and 0.4 (solid line).

interesting is that C_μ for the ML shows a peak below its spinodal. As μ_M increases, the spinodals of the SCL and ML move toward each other (continuous curves). However, the C_μ peak in the ML does not move much, although its height diminishes and eventually saturates with μ_M . Eventually, the spinodals of the ML and SCL meet at a *critical point* for some critical value of μ_M . Above this critical value, the criticality between the ML and SCL disappears (\blacktriangledown). We no longer see any divergence in C_μ (solid curve), but the C_μ

peak at the lower temperature remains intact with its height saturated. It is clear that this peak corresponds to the smoothed out singularity at T_{MC} for finite polymers. This singularity is not due to any singular behavior present in the EL or SCL, but due to that in the ML, which originates at low temperatures. Because of its low-temperature origin, the ML is relatively more ordered than the SCL, which shows in the small values of $x(O)$ and $x(I)$ in the ML. In all the cases we have studied, we have not seen negative expansion coefficients.

To summarize, we have shown that the free volume has no anomalous behavior when the entropy crisis occurs. Surprisingly, its behavior near the MC transition is singular, suggesting that its rapid drop is more closely connected with the dynamic slowing down and the anomalous viscosity associated with the dynamic MC transition. This is another support for identifying T_{MC} with a thermodynamic transition point underlying the dynamic MC transition in polymers. The transition occurs in the ML, and not in the SCL. It is sharp only for infinite polymers, but retains its signature even for finite but long polymers. The ML has very little free volume compared to the SCL. It originates at low temperatures and exists only over a finite temperature range, disjointed from the SCL, if there is too much free volume corresponding to small values of μ_M . The observed spinodals in the ML and SCL, even without any hydrogen bonding in the model, and without negative expansion coefficient, suggest that their presence is more common than is usually thought of. Increasing μ_M increases the temperature range of the ML, which eventually joins with the SCL to give rise to a SCL-ML extension all the way down to the Kauzmann temperature. The location of the specific heat peak associated with the underlying MC transition does not move much throughout this. It is the high monomer density that destroys the spinodals.

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