Rapid Entropy Drop, Kauzmann Catastrophe, and an Apparent Mode-Coupling Transition in Polymers: An Exact Model Calculation on a Husimi Cactus

P. D. Gujrati[1,2] and Andrea Corsi[1]

[1]*Department of Physics, The University of Akron, Akron, Ohio 44325*
[2]*Department of Polymer Science, The University of Akron, Akron, Ohio 44325*

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We identify the *mechanism* behind a rapid entropy drop in the metastable (ML) polymer liquid and clarify the significance of the Kauzmann paradox. We also establish a thermodynamic basis for an apparent critical mode-coupling transition between supercooled (SCL) and ML polymer liquids, and for the ideal glass transition but only in ML. The latter need not *ever* form an equilibrium phase. The crystal can have higher entropy than ML or SCL polymer liquids.

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The glass transition in *fragile* supercooled (SCL) liquids is believed to be a manifestation of a rapid drop in the *configurational entropy* near the Kauzmann temperature T_{K}, and has been a topic of continuous interest for over five decades [1–5]. According to the still unresolved paradox posed by Kauzmann [1], the "extrapolated" entropy $S_{\mathrm{SCL}}(T)$ of the supercooled liquid becomes less than the entropy $S_{\mathrm{CR}}(T)$ of the crystal (CR) at low enough temperatures below the glass transition temperature T_{G}. Most scientists believe [2,4] that $S_{\mathrm{SCL}}(T) \geq S_{\mathrm{CR}}(T)$ below the melting temperature T_{M}, even though there is *no such thermodynamic requirement.* Accordingly, it is conjectured that the system averts the Kauzmann catastrophe by either spontaneous crystallization [1], which we do not consider here, or by an *ideal* glass transition [2–4]. The latter had been justified *only* for polymers [3(a)] in an approximation, which was proven unreliable due to the exact entropy bounds obtained by Gujrati and Goldstein (G-G) [5]. Whether there is a thermodynamic basis [2–4] for the *glass transition* remains one of the most challenging and still unsolved theoretical problems [4], though major progress has been made recently [6–8].

Recent activities [6–8] in which the crystal is *explicitly* suppressed are primarily based on dynamical pictures either directly related to supercooled liquids or borrowed from spin glasses where the unphysical replica trick is extensively used. In addition, it has also become clear recently that there is a "critical" temperature T_{MC}, at which the correlation time diverges as can be seen in the mode-coupling (MC) theory [9]. Therefore, a critical behavior underlying the dynamic slowing down is a tantalizing possibility. Despite the sudden surge of interest, there is still *no* comprehensive understanding of (i) the nature of the SCL which eventually vitrifies and its relationship with CR, (ii) the mechanism responsible for the *rapid entropy loss* near T_{G}, (iii) the nature of the ideal glass transition, and (iv) a possible thermodynamic basis for the critical (and apparently a mode-coupling) transition in SCL's.

Results.—Our aim in this Letter is to advocate a thermodynamic justification of and explanations for all the above phenomena, see Figs. 1 and 2, in a system of *infinitely* long polymer. The system exhibits a first-order melting transition, see (○) in Fig. 1 (inset), at T_{M} between a high-temperature equilibrium liquid (EL) phase, and an equilibrium CR; the latter has *nonzero* entropy in accordance with the G-G bounds [5]. The CR free energy F_{CR0} at $T = 0$ is the *maximum* possible free energy in *equilibrium* over all T. There is a *metastable* liquid (ML) phase that *exists* at *all* temperatures, but has a higher free energy than EL. The latter can be supercooled to yield SCL, which meets ML critically (i.e., *no* latent heat) and terminates at a critical point $T_{\mathrm{MC}} \leq T_{\mathrm{M}}$; see (●) in Figs. 1 (inset) and 2. The correlation length diverges as $T \to T_{\mathrm{MC}}^{+}$ in SCL [$C(T)$ discontinuous] and contributes to critical slowing down [9(b)]. In contrast, $C(T)$ is continuous in ML at T_{MC}. At some temperature $T_{\mathrm{M0}} > 0$, the ML free energy $F_{\mathrm{ML}}(T)$ crosses F_{CR0}, only to come back to it at $T = 0$. Hence, it has a *maximum* at $0 < T_{\mathrm{K}} < T_{\mathrm{MC}}$, where the entropy $S_{\mathrm{ML}}(T_{\mathrm{K}})$ *vanishes.* At $T_{\mathrm{eq}} > T_{\mathrm{K}}$, $S_{\mathrm{CR}} = S_{\mathrm{ML}}$, but $S_{\mathrm{CR}} > S_{\mathrm{ML}}$ between T_{K} and T_{eq}. The Kauzmann catastrophe occurs below T_{K} and not below T_{eq}. Below T_{K}, ML cannot continue due to negative entropy. The implication is that all the states along this part of ML do *not* exist in a thermodynamic sense; these states correspond to

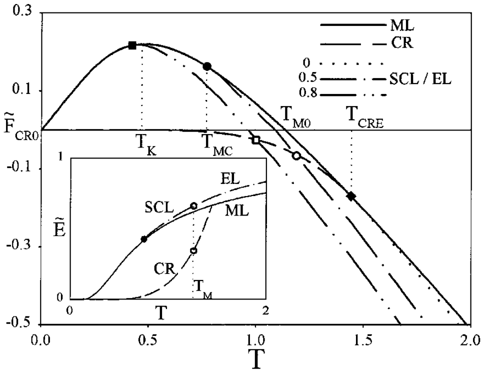

FIG. 1. $\tilde{F}(T) \equiv F(T) - \varepsilon'$ for different states and $a = 0, 0.5$, and 0.8, and $\tilde{E}(T) \equiv E(T) - \varepsilon'$ (inset) for $a = 0.5$. ML (continuous line). CR (dashed line). EL/SCL (dotted, dash-dotted, and dash-dot-dotted lines), T_{MC} (◆, ●, ■), and T_M (◆, ○, □) for $a = 0, 0.5$, and 0.8, respectively.

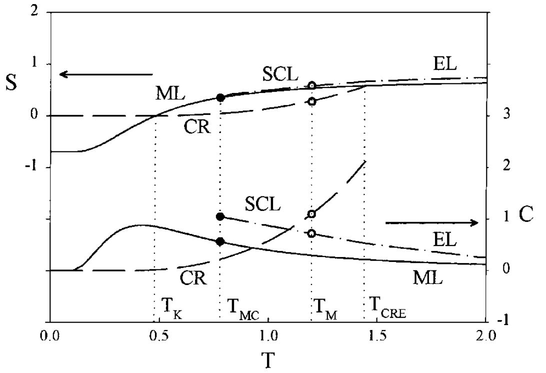

FIG. 2. $S(T)$ (left axis) and $C(T)$ (right axis) for $a = 0.5$; see legend in Fig. 1.

lower energies than at T_K; see Fig. 1 (inset). At T_K, ML gets trapped in one of the thermodynamically insignificant many states of energy $E_K = E_{ML}(T_K)$. Below T_K, it cannot be in states with higher energies, since that would correspond to negative specific heat. It cannot be in lower energy states, as they do not exist. Spontaneous crystallization [1] is not considered as said earlier. Hence for all $T < T_K$, ML remains "frozen" in the "ideal" glass state available at T_K. Since the state of the system does *not* change at T_K, the ideal glass transition is continuous.

Model.—We now proceed to demonstrate these conclusions in an explicit *exact* calculation. We consider the Hamilton walk (HW) limit of a polymer [5], in which it visits every site of the lattice once. For convenience, we consider a square lattice in lieu of a tetrahedral lattice. There are two separate interaction energies to sustain liquid-liquid and melting transitions. It is easy to see that a two-site interaction does not affect the thermodynamics of HW. There is a three-site bending penalty $\varepsilon > 0$ for each of the two possible gauche (g) bonds at each site of the lattice. There is no penalty for a trans bond. This interaction promotes crystallization. The second interaction is a four-site interaction caused by steric effects: energy $\varepsilon' > 0$ for each pair of neighboring parallel bonds. Let N_g denote the number of bends and N_p the number of parallel pairs of neighboring bonds. The energy of interaction is given by

$$\mathcal{E} = \varepsilon N_g + \varepsilon' N_p = \varepsilon(N_g + aN_p), \qquad (1)$$

where $a = \varepsilon'/\varepsilon$. We introduce $w = \exp(-\varepsilon/T)$ and $w' = w^a$ for later use. We also replace T/ε by T, so that the temperature is measured in the units of ε. Volume change upon melting, which has been shown to be important [10], will be considered in a separate publication.

There are four local conformation of HW *at* each site. Each site is shared by two squares Σ and Σ'; Σ is marked by a filled dot close to the site, as shown in Fig. 3. Consider some Σ, and the site near the filled dot. From inside Σ, we look *across* this site into the opposite square Σ' to define the four conformations. They are L, R, and O corresponding to a left turn, a right turn, and an outside turn in Σ', respectively, and an internal turn I within Σ. For $a < 1$, the ground state of the HW at $T = 0$ is, see 1 and 2 in Fig. 3, the one in which all bonds are parallel ($N_p = N$) with no bends ($N_g = 0$), and $F_{CR0} = \varepsilon'$. Because of this, we find $\tilde{F} \equiv F - \varepsilon'$ to be more convenient to use, since $\tilde{F}_{CR0} = 0$ for all ε'. In the ground state, L and R alternate; their respective density l and r equal $\frac{1}{2}$. For $a > 1$, the ground state is a steplike walk, see 3 and 4 in Fig. 3, with the maximum number of bends ($N_g = N$), but no neighboring parallel bonds ($N_p = 0$). This state is described by a sequence *RIRIRI*..., or *LILILI*..., and does not correspond to a crystal. Therefore, we consider only the case $a < 1$.

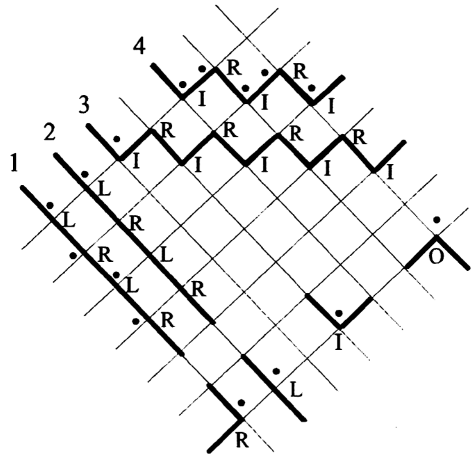

FIG. 3. The states of a site and possible ground states. The dots (•) show the corner of Σ, with Σ' across it. We show the sequence of dots for configurations 1 and 4 of the walk.

The problem is solved exactly on a Husimi cactus, which is a *fixed* structure; see Fig. 1 in Ref. [11(a)], where it is shown that such calculations are more reliable than conventional mean-field calculations and *satisfy* thermodynamics. The exact solution becomes an approximate theory on a square lattice. The cactus is an infinitely large tree, obtained by joining two squares at each corner recursively. It is divided into generations, with the generation number m at each site increasing progressively as we move away from the origin $m = 0$ of the cactus. We follow Ref. [11] closely and introduce, as is the standard practice, partial partition functions $Z_m(\alpha)$ at the mth generation site, given that the state of the walk at the site is $\alpha = L, R, I, O$; $Z_m(\alpha)$ are the contributions of the part of the cactus above this level. We recursively express $X_\alpha = Z_m(\alpha)$ in terms of $Y_\alpha = Z_{m+1}(\alpha)$:

$$\begin{aligned}
X_I &= w(Y_I + 2ww'Y_O)Y_LY_R, \\
X_O &= Y_I^3 + (2Y_I + wY_O)Y_LY_R, \\
X_L &= (wY_L + Y_R) \\
&\quad \times (Y_I^2 + wY_IY_O + w'Y_LY_R + w^2w'Y_O^2),
\end{aligned} \qquad (2)$$

and X_R is given by $L \leftrightarrow R$ interchange in the equation for X_L. We introduce the three ratios $x_m(\alpha) = Z_m(\alpha)/[Z_m(L) + Z_m(R)]$ for $\alpha = L$, I, and O, and $x_m(R) = 1 - x_m(L)$. On an infinite cactus, $x_m(\alpha)$ near the origin approaches its fix-point (FP) solution whose nature determines the bulk behavior of the model. We consider two different *schemes* for the FP. The complete analysis will be presented elsewhere [12]. Here, we will content ourselves with the final results, as the technique is standard.

1. 1-Cycle FP scheme: Here, $x_m(\alpha) \to x_\alpha$ near the origin. We set $x_\alpha = l, i$, and o, for $\alpha = L, I$ and O, and $x_R = r = 1 - l$. We *always* have $l = \frac{1}{2} = r$. For i and o, we have

$$\begin{aligned} i &= w(i + 2ww'o)lr/Q_{LR}, \\ o &= [i^3 + (2i + wo)lr]/Q_{LR}, \end{aligned} \tag{3}$$

where $Q_{LR} = (1 + w)(i^2 + w'lr + wio + w^2w'o^2)$. The solution $i = o = 0$ exists for *all* T and represents ML: $\tilde{F}_{\mathrm{ML}}(T) = -T\ln[(1 + w)^2/2]$. The energy $\tilde{E}_{\mathrm{ML}}(T) = 2w/(1 + w)$ increases monotonically with T, see Fig. 1, and resembles the excitation profiles for the mixed Lennard-Jones system [13(a)] and the two-state model [13(b)]. The specific heat C_{ML} is maximum at $T_{\max} \cong 0.42 < T_K \cong 0.48$, see Fig. 2. For $T > T_{\mathrm{MC}}$, there is another solution EL with $i \neq 0$, $o \neq 0$, see Fig. 1, which merges with ML *critically* at an a-dependent T_{MC} (◆, ●, ■ as a increases), where both phases become identical. In ML, L and R are distributed *statistically.* In EL, I and O are also *statistically* distributed, and EL has more energy and disorder than ML; see the inset in Fig. 1. As $T \to T_{\mathrm{MC}}^+$, o and i continuously vanish in EL; S remains continuous but C has a discontinuity, giving rise to critically and to critical slowing down [9] in the EL ↔ ML transition. In contrast, $C_{\mathrm{ML}}(T)$ remains continuous at T_{MC}, which can make the dominant dynamics in ML and EL very different. In particular, if EL is suppressed and we superheat ML, the observed dynamics should be very different. This is precisely what is observed, see Fig. 2 in Ref. [7(b)], where the fast dynamics (of EL) is suppressed in the model. No critical slowing down is apparent as T is raised above T_{MC}. Kisliuk and co-workers [13(c)] also observe critical dynamics only above and not below T_{MC}, which is consistent with our scenario. Thus, there appears to be a very close parallel between the EL ↔ ML transition here and the MC transition. Being a thermodynamic transition, the specific heat C has a jump at T_{MC} for the EL-ML transition, but is smooth if ML is superheated across T_{MC}. A (first-order) liquid-liquid transition has been seen in Si [13(b)] and supercooled water above certain critical pressure [13(d)].

2. 2-Cycle FP scheme: At $T = 0$, CR contains an *alternating but ordered* sequence of L and R, in addition to having $l = \frac{1}{2}$, but no I and O. This is a 2-cycle pattern in L and R. Thus, higher cycle patterns do not have to be considered. For ML, $l = \frac{1}{2}$ also, but L and R are statistically distributed. One of these distributions must be the crystal state at $T = 0$; indeed, $F_{\mathrm{ML}}(T = 0) = F_{\mathrm{CR}0}$. Despite this, ML immediately above $T = 0$ *cannot* represent CR, as it has negative entropy. To obtain the *alternating* sequence in CR at $T > 0$, the above 1-cycle FP scheme must be modified. To this end, we observe that for $T > 0$, there must be local Gujrati-Goldstein excitations [5,10] creating imperfections by local $L \leftrightarrow R$ interchanges in the ordered $[\ldots LRLRLR \ldots]$ sequence. The excitations change a local string LRL into LLL, or RLR into RRR within a square and require four bends only. [Other excitations, which require (L or R)↔(I or O) on the cactus, *cannot* be done locally and require an infinite amount of energy, and need not be considered.] This means that the local density l or r will no longer be $\frac{1}{2}$. However, if $l > \frac{1}{2}$ at some site, then $r > \frac{1}{2}$ at the next site, followed by $l > \frac{1}{2}$ on the next site and so on. Thus, we look for a scheme that imposes a sublattice structure of two different kinds A and B on the lattice. Set $x_m(L) = l_{\mathrm{A}}$, $x_{m-1}(L) = l_{\mathrm{B}}$, followed by $x_{m-2}(L) = l_{\mathrm{A}}$, $x_{m-3}(L) = l_{\mathrm{B}}$, and so on. We find that

$$l_{\mathrm{A}} = (r_{\mathrm{B}}^2 l_{\mathrm{A}} + w l_{\mathrm{B}}^2 r_{\mathrm{A}})/[2(1 + w)(r_{\mathrm{B}}^2 l_{\mathrm{A}} + l_{\mathrm{B}}^2 r_{\mathrm{A}})], \tag{4}$$

with l_{B} given by A ↔ B interchange; note the a independence. For all T, $l_{\mathrm{A}} = l_{\mathrm{B}} = l = \frac{1}{2}$ is a solution and corresponds to ML. Below $T_{\mathrm{CRE}} \equiv \ln 2$ (◆, Fig. 1), two *new* solutions, equal in energy, *bifurcate* continuously out of ML, such that if $l_{\mathrm{A}} > \frac{1}{2}$, then $l_{\mathrm{B}} < \frac{1}{2}$, or vice versa. This is a 2-cycle FP solution for CR at $T > 0$ with a sublattice structure and is stable. At $T = 0$, $l_{\mathrm{A}} = 1$, $l_{\mathrm{B}} = 0$, or vice versa. All three solutions have the same ground state energy.

The free energy $\tilde{F}_{\mathrm{CR}}(T) = -T\ln[(1 - w^2)^2/(1 - 2w^2)]$ of CR is shown in Fig. 1 and CR coexists with EL at a first-order melting temperature T_{M} (○, □ as a increases) for $a > 0$. Both T_{M} and T_{MC} depend on a, but T_{K}, T_{eq}, and $T_{\mathrm{M}0}$ do *not.*

Ground state.—We now make an *important* observation for $T = 0$. If the correct ground state on the original (here square) lattice is also realizable on the special lattice on which the problem is solved *exactly* (here Husimi cactus), then the ground state energy, which is also the free energy, on the special lattice must be *exactly equal* to that on the original lattice.

The calculation for CR and ML is done exactly on the cactus in different schemes. Both contain the ground state. Hence, the $T = 0$ free energies in both phases are equal. For CR, $F_{\mathrm{CR}}(0)$ is the maximum. For $T < T_{\mathrm{M}0}$, F_{ML} becomes *larger* than $F_{\mathrm{CR}0}$ because it rises faster than F_{CR} as T is reduced, and *its maximum at* T_{K} *is a mathematical necessity* since $F_{\mathrm{ML}}(0) = F_{\mathrm{CR}0}$. Thus, the sudden drop in the entropy S_{ML} near the maximum is also a necessity. We conclude, therefore, that a Kauzmann temperature must exist in a "metastable" state provided *it goes into the ground state* at absolute zero. This is a sufficient but not a necessary condition. Near T_{K}, S_{ML} must vanish linearly, see Fig. 2 for $a = 0.5$; this is also found experimentally. The specific heat C has an upward discontinuity from zero at T_{K}, with C_{ML} decreasing with T. This behavior is also observed by Parisi and co-workers [7(c),(d)]. Also, near

T_K, $S_{CR} > S_{ML}$. This is not a paradox. (For $a \approx 0.8$, even the SCL phase has a corresponding Kauzmann temperature, where its free energy is a maximum, see Fig. 1, and $S_{CR} > S_{SCL}$ near this temperature.)

The possibility of many metastable "states" seen experimentally is due to kinetics. We believe that these states are a manifestation of the above phase ML, though this cannot be demonstrated in our equilibrium calculation. It is certainly possible to construct metastable states, which do not contain the ground state. Such states *cannot* be unique. It is hard to believe that all such states will necessarily give rise to a Kauzmann temperature. However, our calculation also does not throw any light on this issue, as both schemes give unique states at $T = 0$. We must also emphasize the mean-field nature of our calculation in which negative entropy can occur in states that are not true equilibrium states. This will never happen in simulations, but they also cannot probe the ideal glass and the MC transitions because of dynamics slowing down. Thus, our calculation serves a very useful and important purpose in clarifying the subtle equilibrium aspects of SCL's and the glass transition and supplement simulations.

Our final comment is for the case $a \leq 0$. For $a = 0$, our model reduces to the Flory model of polymer melting [10,14], which forms the basis for the Gibbs-Di Marzio conjecture [3(a),5]. For $a < 1$, $\tilde{F}_{ML}$ and $\tilde{F}_{CR}$ are a independent and always meet critically at T_{CRE}, but $\tilde{F}_{EL}$ moves towards lower T with a and slides critically along $\tilde{F}_{ML}$ and crosses $\tilde{F}_{CR}$ so that $T_{MC} \cong 0.768$ (●) and 0.419 (●) and $T_M \cong 1.198$ (○) and 1.009 (□) for $a = 0.5$ and 0.8, respectively. At $a = 0$, $T_M = T_{MC} = T_{CRE}$ (◆), and the "melting" transition becomes *continuous* [10], in contradiction with the Flory calculation [14] and the Gibbs-Di Marzio analysis [3(a)]. There is no SCL. As a is reduced below zero, $T_{MC}(a)$ moves to higher T. This makes ML an equilibrium phase between $T_M = T_{CRE}$ and $T_{MC}(a)$ and can be supercooled; despite this, the melting transition at T_M is *continuous.* This makes the melting in the Flory model a *tricritical* point. This is unexpected, as this possibility has not been considered [5,10]. Continuous melting cannot be identified with first-order melting in real polymers. Thus, $0 < a < 0.8$ seems an appropriate range in real system. Let us consider polyethylene, for which the melting temperature is 400 K. Let us take $a = 0.5$, for which $T_M/T_K = 1.198/0.48$. Thus, the Kauzmann temperature for polyethylene is 160 K, which is 40 K below the usual glass transition around 200 K. Thus, our theory makes reasonable predictions.

We now summarize our results. We propose a model of semiflexible infinitely large polymer (HW), which is solved *exactly* on a Husimi cactus. The model captures the important physics of the problem and demonstrates the thermodynamic basis for an apparent mode-coupling critical transition at T_{MC} between a supercooled liquid and a metastable liquid. The metastable liquid *never* forms an equilibrium state ($a \geq 0$) and cannot be thought of as an "extension" of any equilibrium state, contrary to the supercooled liquid, which is an extension of the equilibrium state EL at $T > T_M$. Our calculation shows for the first time the thermodynamic significance of the MC transition. The ideal glass transition occurs in the metastable liquid and not in the supercooled liquid contrary to the common belief [4]. It is a surprising result. We provide a thermodynamic justification for the rapid drop in the entropy near T_K by arguing for the importance of including the ground state in calculating the metastable free energy. We further argue that the ideal glass transition at T_K is driven by the vanishing of S_{ML} and not by its equality with S_{CR}. We further argue that the metastable liquid is the ideal glass at T_K, and the ideal glass transition is continuous. It is possible for S_{CR} to be larger than S_{ML} and S_{SCL}. We are currently investigating the effects of compressibility and finite chain size.

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