The Kauzmann Paradox Revisited[†]

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Many glass-forming substances display heat capacities for their supercooled liquids that substantially exceed those of the corresponding crystals. Reasonable extrapolation below the kinetic glass transition temperature indicates that the molar entropies of the supercooled liquid and crystal phases would become equal at a "Kauzmann temperature" $T_K > 0$. Furthermore, continuing such extrapolation below T_K to absolute zero suggests that the disordered liquid attains lower entropy than the crystal, in conflict with the third law of thermodynamics (hence the "Kauzmann paradox"). The present study cites data for real substances and results from numerical simulation and theoretical modeling in the temperature−pressure plane to demonstrate that a Kauzmann locus $T_K(p)$ can indeed occur, though not necessarily for all materials. No third-law conflict arises. Also, the analysis provides no support for the concept of an "ideal glass transition" at positive temperature, often mentioned in connection with glass formers. In the event that classical statistical mechanics is applicable to a substance of interest, the low-temperature endpoint of the Kauzmann locus involves the maximum isotropic tension sustainable by spatially uniform amorphous deposits, a state which coincides in pressure and density with the minimum of the $T = 0$ liquid spinodal.

I. Background

Among all of their fundamental properties, the phase transition characteristics of materials occupy a particularly prominent position. Furthermore, those characteristics are often decisive in determining the scientific and technological significance of materials. The first-order melting/freezing transition is perhaps the clearest example, and great importance attaches to how it occurs and how it can be kinetically encouraged or inhibited. The common occurrence of liquid supercooling below the thermodynamic freezing temperature illustrates the latter of these features, and its implications for glass formation and related phenomena form the subject of this paper.

Although the latent heat of fusion causes a liquid at its equilibrium melting/freezing point to inherit a larger entropy than the crystal from which it came, subsequent supercooling reduces that entropy difference on account of the typically larger heat capacity of the liquid compared to the crystal. Simon[1] was perhaps the first to consider in depth the thermodynamic consequences of this situation, in particular surmising what would in principle transpire if kinetic arrest at an experimental glass transition did not intervene during supercooling to absolute zero. However, it was not until more accurate and comprehensive supercooling data later became available to the scientific community that a decisive analysis became possible. The classic and frequently cited review by Kauzmann[2] perhaps can be viewed as the beginning of the present era of the subject. In particular, that work clearly stated the apparently paradoxical implication of extrapolated heat capacities for supercooled liquid and crystal, namely that approach to absolute zero would have the higher enthalpy former possessing lower entropy than the latter. Were this behavior to continue at sufficiently low temperatures, it would result in a liquid with negative entropy, in contradiction to the third law of thermodynamics.[3] Kauzmann's resolution to this apparent paradox was to stress that experiment would always be frustrated either by spontaneous nucleation of the crystal, or by the kinetic arrest of a positive-temperature glass transition, in attempting to carry "equilibrated" supercooled liquids to absolute zero.[2] In any event, one must always be concerned about the intrinsic danger in extrapolating properties into a regime that is forever beyond direct observation.

Nevertheless, the temptation has been strong to declare the outcome of such an in-principle extrapolation. This has been particularly true for theoretical modeling that is not constrained by the reality of experimental kinetic barriers. One class of theoretical models proposes that a higher order "ideal glass transition" should occur at (or close to) the Kauzmann temperature $T_K > 0$, where the isobaric molar entropy difference $\Delta S(T) = S_{liq}(T) - S_{crys}(T)$ vanishes, and below which the system remains in a minimal-enthalpy amorphous state.[4] This proposition would appear to receive support from measurements of supercooled-liquid shear viscosities η and mean relaxation times τ that can often be fitted well to the non-Arrhenius VTF (Vogel−Tamman−Fulcher) form[5]

$$\eta, \tau \approx A \exp\left(\frac{B}{T - T_0}\right) \qquad (1.1)$$

where A and B are suitable constants, and where indeed the divergence temperature T_0 turns out to be close to the calorimetric T_K.[6]

Although experiments on supercooled liquids and their glass transitions are usually performed at atmospheric pressure, exceptions involving elevated pressure p are also available in the scientific literature.[7] This suggests that a "Kauzmann curve" $T_K(p)$, or equivalently $p_K(T)$, of vanishing $\Delta S(T,p)$ should exist for at least some substances. If the presumption is correct that an ideal glass transition is involved in the T,p plane, this curve should be its locus.

Gibbs and DiMarzio[8] produced a theory for polymer melts, based on the Flory−Huggins treatment of chain statistics,[9] that exhibited a vanishing configurational entropy at a positive temperature. This development has often been taken as support for the ideal glass transition concept, not only for polymers, but for low-molecular-weight substances as well. Adam and Gibbs[10] subsequently extended the Gibbs−DiMarzio concepts to advance a connection between calorimetric measurements and various relaxation times τ (often approximately proportional to the shear viscosity η), by introducing the idea of a temperature-dependent cooperatively rearranging molecular region in the supercooled liquid. Specifically, they proposed

$$\eta(T), \tau(T) \approx C \exp\left(\frac{D}{TS_{\text{config}}}\right) \qquad (1.2)$$

where C and D would be pressure-dependent constants for each substance of interest, and S_{config} is a "configurational entropy". The original view was that $S_{\text{config}} \approx \Delta S$, so that the Adam−Gibbs expression could provide a divergence at an ideal glass transition in agreement with the VFT expression (1.1). However, in addition, it offered a suggestive picture of how flow and relaxation processes occur in deeply supercooled liquids by virtue of localized molecular rearrangements within a static surrounding medium. A limitation of the Adam−Gibbs theory is that it provides no information on the size of the cooperatively rearranging regions.

Although the precise definition of "configurational entropy" was lacking in the original Adam−Gibbs treatment, more recent developments usually have associated this concept with the energy-dependent degeneracy of "inherent structures".[11−13] These are mechanically stable configurations of all of the system's particles, or equivalently the local minima of the many-particle potential energy function. The full entropy function in this representation then consists of two parts:

$$S = S_{\text{config}} + S_{\text{vib}} \qquad (1.3)$$

where S_{vib} arises from motions that displace the many-body system away from inherent structures, but which are confined to the basins of attraction of those inherent structures.

A theoretical argument has been advanced[14] indicating that, for substances of low molecular weight, S_{config} alone cannot produce an ideal glass transition as defined above. Furthermore, it is difficult to construct a scenario in which intrabasin vibrational entropy S_{vib} could induce such a transition. However, the argument presented was not sufficiently powerful to cover the cases involving polymeric substances with unbounded molecular weights. Furthermore, it did not exclude the possibility that ΔS, the difference in total entropies between supercooled liquid and crystal phases, could go to zero and become negative over a temperature range, on the way toward absolute zero.

Other approaches have appeared in the literature developing the thesis that no underlying phase transition should occur on equilibrated supercooling to absolute zero. One of these, due to Kivelson and co-workers,[15] postulates a central role played by frustration in the molecular interactions within the amorphous phase. Another, due to Johari,[16] provides smooth extrapolations to absolute zero of measured heat capacities in such a way that a positive Kauzmann temperature T_K is avoided, in a manner similar to Simon's early suggestion.[1]

The present paper is structured as follows. Section II examines the cases of the helium isotopes at low temperature, concluding that indeed this substance possesses a Kauzmann curve $T_K(p)$. Section II also considers a polymeric material for which the available melting curve data also strongly suggest that it possesses a Kauzmann curve as well. Section III discusses two simple classical statistical models (hard and soft spheres), for both of which Kauzmann curves can be calculated. Section IV extends the analysis to the metastable negative-pressure (tension) regime, and establishes a nonobvious connection between the limiting low-temperature spinodal curve and the Kauzmann locus. Section V contains a summary of our conclusions and a discussion of several open scientific questions.

II. Kauzmann Curves for Selected Materials

A natural starting point for a discussion of Kauzmann curves involves consideration of real-substance examples that exhibit discrete Kauzmann points in their equilibrium phase diagrams. Metastable extensions of the phases involved serve then to connect those points with a curvilinear Kauzmann locus. The discrete points at issue occur at maxima or minima of the melting curve $p_m(T)$ in the T,p plane. The Clapeyron equation[17]

$$dp_m/dT = \Delta S/\Delta V \qquad (2.1)$$

requires that if the volume change ΔV for the transition is nonzero at a $p_m(T)$ extremum, then the entropy change ΔS must vanish there; i.e., it must perforce be a Kauzmann point.

The phase diagrams of the helium isotopes He^3 and He^4 provide a clear-cut pair of examples. Admittedly these are substances whose properties are dominated by quantum effects, hence they show no obvious tendency to form solid glasses, and in this respect they differ from the conventionally discussed glass formers. However, all substances exhibit quantum effects to some extent, which in the case of polyatomic molecules may most strongly be manifest as quantized high-frequency intramolecular vibrations. It should also be kept in mind that all amorphous solids apparently contain a small positive concentration of two-level localized degrees of freedom, whose quantized low-temperature behavior dominates heat capacity and contributes to thermal conduction and ultrasound absorption.[18] The helium examples thus fit into the larger quantum context for all materials, and form a relevant and illuminating part of the full Kauzmann curve picture.

Figure 1 schematically illustrates the melting curves for both isotopes.[19] Although there are significant quantitative differences between the two cases, their respective $p_m(T)$ show single relative minima at a positive temperature (approximately 0.3 K and 29.8 bar for He^3, 0.8 K and 26.2 bar for He^4).[19] Furthermore, both melting curves have zero-slope positive-pressure local maxima at $T = 0$, where the respective systems are necessarily in their ground states at all pressures. Throughout the entire melting range considered, the melting volume is positive:

$$\Delta V = V_{\text{liq}} - V_{\text{crys}} > 0 \qquad (2.2)$$

Consequently, the Clapeyron equation (2.1) demands that $\Delta S = 0$ at both $T = 0$ and at the melting curve minima; i.e., these are legitimate Kauzmann points. The $T = 0$ maxima obviously possess this property, because they represent structural shifts in the pure ground states, for which entropy vanishes. For both
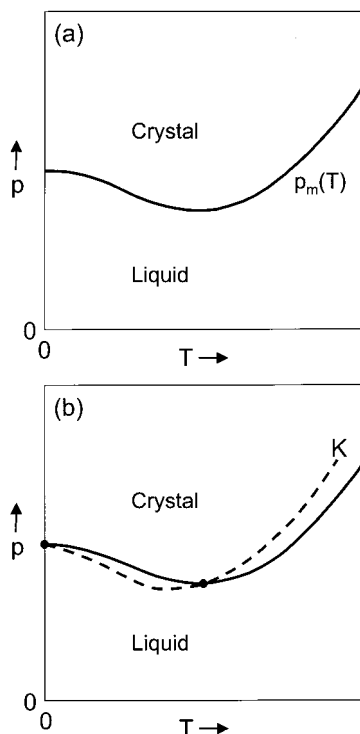
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Figure 1. (a) Schematic diagram illustrating the melting curves for the isotopes He[3] and He[4] in the T,p plane. Although significant quantitative differences between the two cases exist, both display maxima at $T = 0$ and single minima at $T > 0$. (b) Same as (a), but with inclusion of the inferred Kauzmann curve $p_K(T)$, denoted by "K".

isotopes, the temperature range between $T = 0$ and the melting-curve minimum at T_{min} has

$$dp_m(T)/dT < 0 \qquad (2.3)$$

and over this range freezing of the liquid occurs by absorbing heat, the reverse of the usual situation. Consequently, the crystal in equilibrium with the liquid along this portion of the melting curve has higher entropy than the liquid.

The physical explanation for inequality (2.3) and the reverse-melting phenomenon rests with the spectra of low-lying excitations present in the liquid and crystal phases at low temperature. In He[4] these are just phonons, i.e., quantized sound waves. The crystal phase of He[4] is an elastic solid, and consequently it can support both longitudinal and transverse phonons.[20] However, the liquid can only support longitudinal phonons.[21] Consequently, the crystal has a substantially larger phonon density of states than does the liquid, and this is reflected in the magnitudes of the low-T heat capacities:

$$C_p^{(liq)}(T,p) = \gamma^{(liq)}(p)T^3 + O(T^4)$$

$$C_p^{(crys)}(T,p) = \gamma^{(crys)}(p)T^3 + O(T^4) \qquad (2.4)$$

where

$$0 < \gamma^{(liq)}(p) < \gamma^{(crys)}(p) \qquad (2.5)$$

The corresponding entropies are the following:

$$S^{(liq)}(T,p) = \frac{1}{3}\gamma^{(liq)}(p)T^3 + O(T^4)$$

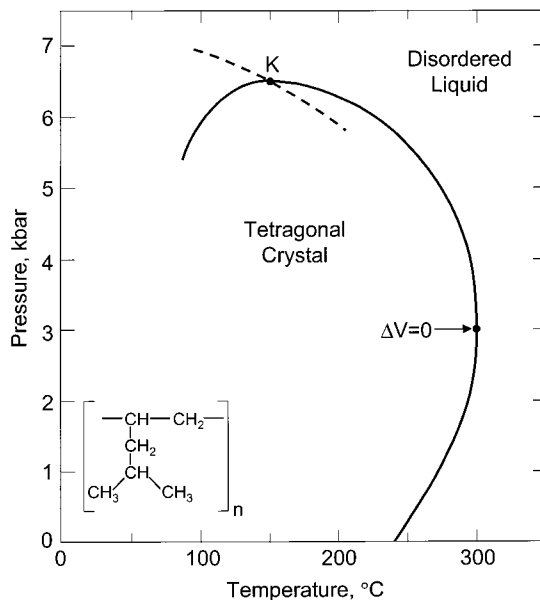$$S^{(crys)}(T,p) = \frac{1}{3}\gamma^{(crys)}(p)T^3 + O(T^4) \qquad (2.6)$$

Figure 2. Melting curve in the T,p plane for isotactic poly(4-methylpentene-1), "P4MP1", adapted from refs 22−25.

These, in connection with inequalities (2.5), indicate that between absolute zero and T_{min} entropy increases upon freezing liquid He[4]. The same phonon density-of-states consideration applies to He[3] as well, but it is believed that differences in nuclear spin couplings in the two phases of this lighter isotope also contribute to development of its melting-curve minimum.[19b]

If the two Kauzmann points on the melting curve are to be incorporated in a Kauzmann curve $p_K(T)$, this curve must deviate from $p_m(T)$ away from those points, and therefore must require one of the two phases to be in a metastable state. It is easy to convince oneself that, below T_{min}, this deviation must take p_K-(T) into the equilibrium liquid-phase region and require a metastable undercompressed (or supercooled) crystal. Above T_{min} the situation is reversed, with equilibrium crystal and supercooled (or overcompressed) liquid. The inferred $p_K(T)$ position appears in Figure 1b. Insufficient data are currently available to trace out the continuation of this Kauzmann curve to high T and p.

The second relevant example is an organic polymer, isotactic poly(4-methylpentene-1), P4MP1. Extensive experimental work has been devoted to establishing the physical properties of this material.[22−25] The average molecular weight M_w reported in the studies of refs 22−25 is 250 000.[24] Although significant breadth of the molecular weight distribution was present ($M_w/M_n = 4.0$[24]), such a small fraction of the monomer units occur at or near the chain ends of this high polymer that the measured phase behavior should be very close to that of the hypothetical zero-breadth-distribution polymer. It might be stressed in passing that P4MP1 contains a high density of covalent C−H bonds (12 per monomer unit), for which the vibrational stretch frequencies typically fall in the range 2500−3500 cm^{-1}. By contrast, thermal energy k_BT at room temperature is only about 200 cm^{-1}, so indeed these degrees of freedom would be strongly quantized at, and well above, room temperature.

Figure 2 shows the relevant part of the P4MP1 phase diagram. It exhibits an unusual shape for the region occupied by the equilibrium crystal (tetragonal). In particular, the melting curve $p_m(T)$ is a multiple-valued function at high temperature, with a maximum melting/freezing temperature occurring at about 300 °C and 3 kbar. At this point the volume of melting ΔV passes through zero, changing from the usual positive sign at low

pressure to the unusual (but not unprecedented) negative sign at high pressure. Otherwise, the phase transition remains first order along this portion of the melting curve, with a positive latent heat. This kind of melting-temperature maximum has been reported for other materials, one example of which is phosphorus.[26] It is also known to appear in the phase diagrams of some theoretical models.[27]

The focus of interest here is the point of maximum pressure along the melting curve. This occurs at about 150 °C and 6.5 kbar. Because the melting volume ΔV does not vanish there, the Clapeyron equation (2.1) requires that the entropy of melting $\Delta S = 0$. Consequently this meets our definition of a Kauzmann point, and has been so labeled ("K") in Figure 2. The reader should be warned, however, that direct experimental observation of this point is hindered and obscured by the tendency of the P4MP1 system to enter another crystal phase (with hexagonal symmetry).[22-25] Nevertheless, one can legitimately imagine circumstances for which nucleation of that distracting transition has been inhibited, leaving just the liquid and tetragonal phases to compete for relative thermodynamic stability. It is this conceptually simplified circumstance for which we identify a Kauzmann point.

Figure 2 indicates qualitatively how a Kauzmann curve (dashed) must presumably be placed, passing through the point just located, but also entering the stability regions for each of the two phases. The situation is analogous to that of the heliums, with the curve residing in the crystal region when melting is "normal", but residing in the liquid region when "inverse melting" occurs. For temperatures above that of the Kauzmann point at the maximum melting pressure, the liquid must be isobarically supercooled to attain the lower entropy of the solid. Contrarily, for temperatures below that of the Kauzmann point where the crystal in equilibrium with the liquid has the higher entropy (and presumably the higher heat capacity as for the helium isotopes), the crystal must be metastably overcompressed to have its entropy brought into equality with that of the liquid.

Evidently, the reason for existence of the melting-pressure maximum for P4MP1 lies in its molecular structure, and the ability of its isotactic chains to pack next to one another. The negative values of ΔV around that maximum, the Kauzmann point, indicate that the ordered chains in the crystal enjoy extra room for motion of at least a portion of the molecule in comparison with the disordered, and denser, liquid. Yet both are at the same pressure at the Kauzmann curve, by definition. This strongly suggests that crystalline P4MP1 in this region of the p,T plane has significantly higher vibrational entropy than that of the liquid, perhaps mostly associated with motions of the side chains.

Historical accuracy and completeness requires mentioning that Tammann in 1903 anticipated the possibility that some substances might indeed display $p_m(T)$ maxima of the sort just described.[28]

In closing this section, we wish to stress that the possibility of a Kauzmann locus along which $\Delta S = 0$ and the possible existence of an ideal glass transition are logically disconnected. The rationales that have been outlined here for the presence of Kauzmann curves for the helium isotopes and for P4MP1 carry no implication for a positive-temperature ($T_0 > 0$) singularity at which configurational entropy of the supercooled liquid vanishes and at which relaxation times and shear viscosity diverge. In this respect the present analysis is consistent with those offered in refs 14−16.

III. Theoretical Models

Theoretical many-body models offer a view of Kauzmann curves complementary to that of the experimental examples discussed in the preceding section II. The first to be considered is the classical rigid-sphere model, which has been the object of many analytical and simulational studies. It is an appropriate starting point for the present section on account of the elementary way that temperature and pressure are related, namely direct proportionality.

Under conditions of thermal equilibrium, the rigid-sphere model under compression from the dilute gas limit is known to exhibit a first-order freezing transition to a face-centered cubic crystal. This crystal persists up to the close-packed limit, at which the reduced density attains the value

$$\rho a^3 = 2^{1/2} \qquad (3.1)$$

Here ρ is the number density N/V, and a is the rigid-sphere distance of closest approach. The values of the coexisting-phase reduced densities at the melting/freezing transition are the following:[29]

$$(\rho a^3)_{\text{fluid}} \cong 0.943$$

$$(\rho a^3)_{\text{fcc}} \cong 1.04 \qquad (3.2)$$

while the reduced pressure in this state of coexistence is

$$pa^3/k_B T \cong 14.3 \qquad (3.3)$$

and the melting entropy at this transition, on a per-particle basis, is

$$\Delta S/Nk_B \cong 1.16 \qquad (3.4)$$

Provided that caution is exercised to avoid crystal nucleation, the rigid-sphere fluid can be compressed metastably beyond the equilibrium freezing density, with rapidly rising pressure and rapidly decreasing rate of self-diffusion.[30,31] It is legitimate to inquire about the quantitative properties of an equilibrated fluid subject to constraints which in principle, at least, prevent nucleation and subsequent crystal growth.[32,33] It is in that spirit that we now investigate the possibility of a Kauzmann point linking the overcompressed metastable fluid and the fcc crystal above the transition pressure. If indeed such a point could be located, it would lie in the p,T plane on a linear Kauzmann curve of the form

$$p_K(T) = CT \qquad (3.5)$$

where C is the appropriate positive constant.

Closed-form pressure equations of state are available for both the fluid and crystal phases of the classical rigid-sphere model. For our present purposes of illustration, we have chosen the Carnahan−Starling equation[34] to represent the equilibrium and metastable fluid ($y = \pi\rho a^3/6$):

$$p/\rho k_B T = \frac{1 + y + y^2 - y^3}{(1 - y)^3} \qquad (3.6)$$

while Speedy's equation[35] serves the equivalent role for the crystal ($z = 2^{-1/2}\rho a^3 = 3 \times 2^{1/2}y/\pi$):

$$p/\rho k_B T = \frac{3}{1 - z} - \frac{0.5921(z - 0.7072)}{z - 0.601} \qquad (3.7)$$

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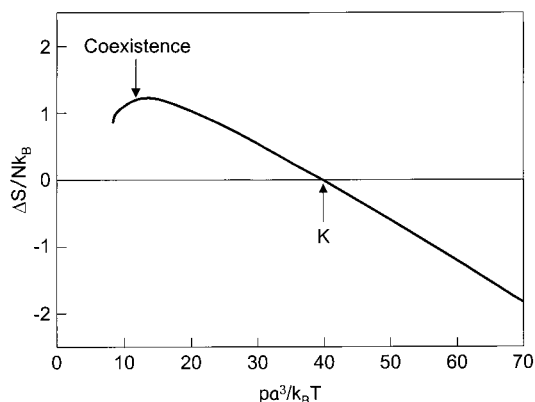*J. Phys. Chem. B, Vol. 105, No. 47, 2001* **11813**

Figure 3. Entropy difference between the rigid-sphere fluid and fcc crystal phases, plotted vs the common reduced pressure. Calculations were based on the Carnahan−Starling[34] and Speedy[35] equations of state. The point (K) at which this entropy difference vanishes is identified as a Kauzmann point.

By using the thermodynamic identity

$$-\frac{1}{\rho^2}\left(\frac{\partial p}{\partial T}\right)_\rho = \left(\frac{\partial S/N}{\partial \rho}\right)_T \qquad (3.8)$$

along with the ideal-gas entropy expression, one finds that the Carnahan−Starling fluid entropy is

$$S/Nk_B = \ln\left(\frac{ea^3}{\lambda_T^3}\right) + \ln\left(\frac{\pi e^3}{6}\right) - \ln y - \frac{2}{1-y} - \frac{1}{(1-y)^2} \qquad (3.9)$$

in which the mean thermal deBroglie wavelength has been denoted by λ_T. Speedy has supplied the crystal entropy expression corresponding to his pressure equation (3.7):[35]

$$S/Nk_B = \ln\left(\frac{ea^3}{\lambda_T^3}\right) - 2.8776 - 2.3033 \ln z + 3 \ln(1-z) - $$
$$0.10463 \ln(z - 0.601) \quad (3.10)$$

With these closed-form estimates for the rigid-sphere thermodynamic functions, it is a straightforward numerical task to search for a Kauzmann point, at fixed temperature, where the pressure and entropy of the two phases are simultaneously equal.[36] In fact, these equations do lead to such a solution. Figure 3 shows the predicted values of $(S_{fluid} - S_{crys})/Nk_B$ plotted against the common reduced pressure for the two phases.

Although this relative entropy is close to its maximum at the predicted coexistence point, further compression causes it to decline and to change sign at the Kauzmann point:

$$p_K(T)a^3/k_B T \equiv Ca^3/k_B \cong 39.69 \qquad (3.11)$$

The reduced densities of the metastable fluid and the crystal that yield this point are found to be

$$(\rho a^3)_{K,fluid} \cong 1.192$$

$$(\rho a^3)_{K,crys} \cong 1.279 \qquad (3.12)$$

Although the numerical results (3.11) and (3.12) depend on the choice of fluid and crystal equations of state, available evidence[36] suggests that reasonable alternative choices would lead to the same qualitative conclusion. One then must consider the question of how such an isobaric equality of entropies can

arise between an "ordered" crystal and a "disordered" metastable fluid. Evidently the explanation resides with the motional freedom available to the spheres in the two types of environment. The geometric packing inefficiency of the disorganized amorphous fluid leaves relatively little room for local free motion (both individual and collective). By contrast, the more efficient periodic crystal packing permits substantially more such motions. Consequently, the crystal receives a significant positive entropy contribution relative to the fluid, a distinction that magnifies under increasing compression. However, this rationale is not a simple and straightforward argument, because the comparisons refer to a condition of equal pressures but unequal densities (eq 3.12) for the two phases.

Although it probably has no decisive implication for the present investigation, an important open question regarding the rigid-sphere model deserves mention in passing. This concerns the location of the density at which the pressure of the metastable fluid should diverge to $+\infty$. The divergence density cannot exceed the close-packed value shown in eq 3.1 above, of course (but note that the Carnahan−Starling approximation does!). However, it remains unresolved whether in principle the divergence occurs at a lower-than-close-packed density corresponding to some kind of irregular packing, or alternatively whether the "fluid" constraint permits continuous approach to close packing via a sequence of structures containing larger and larger crystalline domains.

The rigid-sphere model may be viewed as a limiting case for the "soft-sphere" family of models. This family is distinguished by pair interactions of the generic form $\epsilon(a/r_{ij})^n$, where ϵ and a are energy and length units, and $n > 3$ is required to ensure the existence of proper extensive thermodynamics. Allowing $n \to +\infty$ generates the rigid-sphere case. For any real n satisfying the inequality above, the intensive thermodynamic quantities can be expressed simply as functions of a single scaling variable:[37]

$$z = (\beta\epsilon)^{3/n}\rho a^3 \qquad (3.13)$$

In particular, the pressure and energy per particle have the following forms:

$$p/\rho k_B T = 1 + u_n(z)$$

$$E/Nk_B T = \frac{3}{2} + \frac{3u_n(z)}{n} \qquad (3.14)$$

where $u_n(z)$ is analytic at the origin, with a power series that generates gas-phase virial coefficients for the model. Notice that, in the rigid-sphere limit, z reduces simply to ρa^3. The fluid and crystal phases for the soft-sphere models correspond to distinct branches of the function $u_n(z)$; a short third branch spans the coexistence region for the first-order phase transition between fluid and crystal. Using either of eqs 3.14 as a starting point, thermodynamic integration leads to an expression for the entropy:

$$S/Nk_B = 5/2 - \ln(\rho\lambda_T^3) + (3/n)u_n(z) - \int_0^z [u_n(y)/y]\,dy \qquad (3.15)$$

The pressure and entropy expressions (3.14) and (3.15) for the soft-sphere models can be used to search for the existence of Kauzmann curves, provided that sufficient information is available to specify the $u_n(z)$ fluid and crystal branches. In fact, these models have been carefully investigated by computer simulation,[37−39] with sufficient information now available to
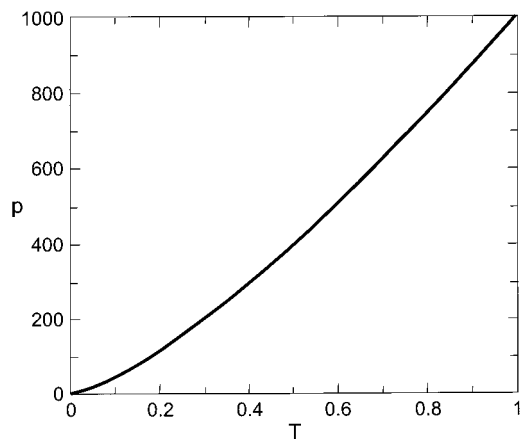
Figure 4. Kauzmann curve calculated for the $n = 9$ soft-sphere model (reduced temperature and pressure units). The densities of the fluid and crystal pairs (with equal pressures and entropies) increase monotonically along the curve moving away from the origin.

approximate the u_n branches with reasonable accuracy. For the specific case $n = 9$, we have found that a semi-infinite Kauzmann curve indeed does exist in the T,p plane, passing continuously from the origin to infinity in the first quadrant.[36] Figure 4 shows our result. In contrast to the linear Kauzmann locus (3.5) for the rigid-sphere limit, the $n = 9$ locus has positive curvature. The densities of both phases increase monotonically from zero to $+\infty$ along this Kauzmann curve, passing from the origin upward and to the right. As one might reasonably expect, the density of the crystal along the Kauzmann locus is always slightly larger than that of the equal-entropy metastable fluid, a conclusion similar to that of eqs 3.12 for rigid spheres.

Evidently the vibrational entropy for the $n = 9$ case is sufficiently lower in the fluid than in the crystal along the Kauzmann curve that it overcomes the configurational disorder discrepancy. By itself the latter would certainly place the fluid at higher entropy than the crystal. Although we have not specifically investigated the existence and nature of Kauzmann curves for other values of the interaction exponent n, it is natural to suppose that semi-infinite curves in the first p,T quadrant, emanating from the origin, would be found for all $n > 3$. If this is the case, then the same comment about the contrasting roles of vibrational and configurational entropy apply in this wider context. In this context it must always be understood that the rigid-sphere model is a very singular limit, for which the basic concepts of "inherent structure", "basin of attraction", and "intrabasin vibrational motion" require very careful interpretation.[40]

IV. $T = 0$ Limiting Spinodal

Although they are nontrivial, the simple theoretical models considered in section III suffer from the obvious failure to include realistic attractive forces that operate in all real materials. In particular, attractions cause real material systems to remain in a condensed state at absolute zero temperature and vanishing pressure, and to have the capacity to enter metastable states of isotropic tension (negative pressure). These features raise obvious questions about how the presence of attractive interparticle interactions might influence the existence and shapes of Kauzmann curves in the T,p space, extended to include negative pressures.

Simulational studies (within the classical statistical mechanical regime) of several models that incorporate both repulsive and attractive interparticle forces reveal that isochoric mapping of liquid configurations onto inherent structures, when carried out

over a wide density range, produces a pressure curve vs density that is essentially equivalent to the absolute-zero limiting isotherm for the supercooled liquid, $p_{\text{liq}}(\rho, T \to 0)$. This limiting isotherm passes through a deep minimum at a distinguished density ρ_S that is virtually coincident with the $T \to 0$ endpoint of the spinodal curve.[39,41–43] For inherent structure mappings carried out from the liquid at $\rho \geq \rho_S$, the resulting amorphous inherent structures are spatially uniform; mappings at $\rho < \rho_S$ are spatially nonuniform, exhibiting irregular cracks, voids, or tunnels. Consequently, ρ_S locates amorphous particle packings of maximal mechanical strength with respect to isotropic tension. Equivalently, ρ_S is a natural lower density limit, below which the substance of interest cannot exist as a homogeneous glass or amorphous deposit. The maximal tensions $p_{\text{liq}}(\rho_S, T \to 0)$ are material specific, but in magnitude tend to be many times the critical pressure. Because points on a Kauzmann curve require equality of pressure for crystal and amorphous phases, $p_{\text{liq}}(\rho_S, T \to 0)$ necessarily sets a lower limit on the pressure of that curve. However, without further analysis it is not clear that the Kauzmann curve actually could attain that limit.

Within the context of theoretical modeling, the mean-field approximation affords a useful way to append attractions to a dense many-particle system with repelling interactions. This approximation formally becomes exact if those attractions are long-ranged but everywhere weak. However, even for relatively short-ranged and moderately strong attractions (such as dispersion interactions), the repulsive portion of the total potential dominates the short-range particle packing order, and the mean-field estimate of attractive interaction effects continues to be relatively reliable for thermodynamic properties.[44]

In the presence of additional mean-field attractions, the soft-sphere pressure and energy expressions shown above in eqs 3.14 become modified to the following:

$$p/\rho k_B T = 1 + u_n(z) - \alpha \rho / k_B T$$

$$E/N k_B T = \frac{3}{2} + \frac{3 u_n(z)}{n} - \frac{\alpha \rho}{2 k_B T} \qquad (4.1)$$

where the u_n branches and z are defined as before, and $\alpha > 0$ measures the strength of mean-field coupling. With such attractions present, the system can now exhibit vapor−liquid condensation and a critical point. The former entropy expression (3.15) continues to apply in the presence of mean-field attractions. Increasing α continuously from zero will cause Kauzmann pairs of metastable fluid and crystal states that share the same pressure and entropy to shift continuously in density. Among the shifted pairs will be one exhibiting the lowest (most negative) pressure. An obvious issue is how this pair relates to the $T = 0$ liquid spinodal that develops in the presence of the appended attractions.

A previous publication[39] has examined exactly that issue for the $n = 9$ soft-sphere model with mean-field attractions. A striking conclusion, illustrated schematically in Figure 5, was that the $T = 0$ terminus of the Kauzmann curve was coincident with the spinodal minimum point at $p_{\text{spn}}(\rho_S)$; however, no explanation for this coincidence was offered in ref 39. It has also been pointed out that the same phenomenon occurs more widely, specifically when mean-field attractions are added to the rigid-sphere and the hard-dumbbell (rigid diatomic) models.[36,39] By implication, we expect the same behavior to obtain for other soft-sphere n values as well, at least with mean-field attractions.

This naturally leads to the question of whether the zero-temperature spinodal minimum also serves as the Kauzmann
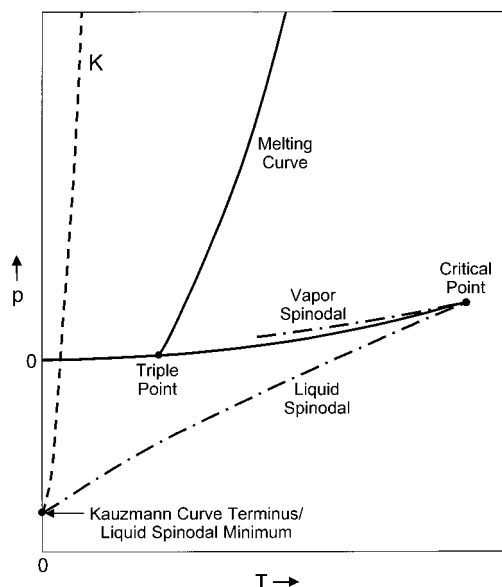
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Figure 5. Schematic plot in the temperature−pressure plane of the equilibrium coexistence curves (solid lines), spinodals (dot−dashed lines), and the Kauzmann curve (dashed line) for the r^{-9} soft-sphere model with additional mean-field attractions (ref 39).

curve terminus when more realistic short-range and possibly direction-dependent and nonadditive attractions are present. The following argument suggests that indeed this is the case. First observe that the maximally strong amorphous deposits present at the spinodal minimum must be devoid of weak spots (e.g., low-density, poorly bonded regions), at least to the extent that the noncrystalline constraint permits. Such weak spots would be the initiating points of mechanical failure. Thus, approach to the spinodal minimum entails a new constraint on the available inherent structures. This may involve elimination of regions within the glassy medium that near the glass transition temperature can be identified experimentally as dynamic heterogeneities;[45,46] such weak spots would naturally exhibit an enhanced mobility under thermal agitation, and appear to underlie the low-temperature failure of the Stokes−Einstein relation.[47] By limiting the number of qualifying inherent structures, the configurational entropy S_{config} is necessarily reduced, and since the constraint selects that inherent structure uniquely qualified to resist fracture, this suggests that $S_{config} \cong 0$, the same as for the crystal at $T = 0$. Following a recent argument due to Martinez and Angell that configurational and vibrational entropies are proportional to one another,[48] we can assume that the vibrational entropies for the two phases become virtually equal as they approach their respective states of isotropic tension p_{min}. This implies that this $T = 0$ pair constitutes a Kauzmann pair. No pair can exist in a greater state of tension, so this must locate the terminus of the Kauzmann curve in the T,p plane.

V. Conclusions and Discussion

By citing a combination of experimental phase diagrams, mean-field model calculations, and theoretical arguments, this paper proposes that many substances display "Kauzmann curves" in their T,p planes, locating crystal−liquid phase pairs with equal pressures and entropies. We do not claim here that such curves exist for all substances and models, but the available evidence suggests that this may not be a rare occurrence. Within the context of classical statistical mechanics, models with particles that exert simple repelling forces (e.g., rigid and soft

spheres, hard dumbbells) appear to possess Kauzmann curves that involve equilibrium crystal and metastable fluid pairs as contributing states. Furthermore, appending attractive forces to those simple models continues to produce Kauzmann curves. In these latter circumstances of repelling and attracting interactions, the $T = 0$ terminus of the Kauzmann curve involves an amorphous inherent structure in a state of maximal isotropic tension, which is a minimum in the $T = 0$ liquid spinodal curve, and the lowest density state at which a spatially uniform glass can exist.

The helium isotopes have been cited as examples with discrete points on their melting curves that satisfy the Kauzmann criteria. Furthermore, these discrete points can credibly be connected by a continuous Kauzmann locus that penetrates the stable liquid region of the T,p phase plane at low temperature, but crosses over into the stable crystal region at higher temperature. The crossing point, consistent with the Clapeyron relation (2.1), is a local minimum of the melting curve. On account of the extreme quantum characters both of He^3 and He^4, neither of these substances is able to participate in the classical statistical coincidence of the Kauzmann terminus and the liquid spinodal minimum; rapidity of tunneling processes eliminates the possibility of creating solid amorphous deposits (glasses) of helium that could be put in a state of tension. It would be very illuminating to pursue a future theoretical project that determines how the phase diagrams and Kauzmann curves of the boson and fermion "heliums" evolve as the particle masses are continuously increased to large values, at which point classical statistical mechanics becomes applicable and solid amorphous particle packings have operational significance.

It is important to understand (as stressed above) that the existence of a Kauzmann locus is not equivalent to the existence of an ideal glass transition. This logical disconnection applies whether quantum or classical statistical mechanics is the appropriate representation. In fact, none of the experimental, simulational, or theoretical evidence cited in this paper points to the presence of any ideal glass transition in any substance at positive temperature.

A recent paper by Sastry[49] has presented simulational results for a frequently used classical model glass former that consists of an approximately 80−20 binary mixture of inequivalent Lennard-Jones particles.[50] The numerical results obtained in that Sastry study included determination of liquid-phase spinodal curves, and free energies over wide ranges of temperature and density. These results were interpreted so as to seemingly contradict the proposition advanced here and in ref 39 that the $T = 0$ Kauzmann terminus and the $T = 0$ spinodal minimum involve the same amorphous state. However, it must be pointed out that the crystal structure or structures for this binary mixture have never been determined, to the best of our knowledge; in fact, the composition examined may not correspond closely to a stoichiometric crystal at all, but rather to a eutectic composition.[50a] Consequently, it is not yet possible to apply the Kauzmann criteria of equal pressure and entropy to crystal and liquid phases as required in our approach. Instead, Sastry employs a "glass transition" criterion based solely on the liquid free energy. The result of this alternative requirement generates novel and valuable information about the binary glass-forming model. However, it is an independent analysis that does not contradict the approach presented above in section IV.

The phase pairs that have been considered above for the presence of Kauzmann loci have all involved crystals on the one hand, and isotropic fluids (liquids) on the other hand. Of course this has been the traditional emphasis. However, such

investigations can in principle be widened to encompass other phase pairs, one of which is metastable, but both of which have identical pressure and entropy. Examples of such phase pairs that may possess Kauzmann loci might be (a) crystal, liquid crystal; (b) liquid crystal, isotropic liquid; (c) crystal polymorph pairs that interconvert by a first-order phase transition; and (d) phase pairs involving at least one quasicrystal. At present little or no attention seems to have been devoted to these possibilities, but they may be worthy objects for future research.

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