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Melting and its relation to molecular orientations in the fluid and solid phases of N_2 and CH_4[†]

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A comparison of recent melting data for N_2, CH_4, and Ar suggests that there probably is greater local orientational order in the dense fluid phases of N_2 and CH_4 than in their respective solids near melting. The possible nature of this local orientational order is discussed.

The orientations and rotations of simple molecules in solids and fluids have long been subjects of interest, and speculations on the extent of orientational correlations in both phases are abundant.[1] The melting transition, where solid and fluid are in equilibrium, can provide a considerable amount of information about how the two phases differ with regard to such correlations. Recently, complete sets of accurate melting data[2] have become available for methane (CH_4) and nitrogen (N_2) over wide ranges of temperature and pressure. These data permit a detailed comparison with the melting properties of the simple monatomic substance argon (Ar), for which extensive melting data are also available,[3] and for which the thermodynamic behavior at the melting transition is at least partially understood.[4] Such a comparison as described below indicates that the molecular orientations do indeed have significant effects on the melting properties, and provides some insight into the nature of the molecular orientational correlations in the fluid and solid phases.

I. CORRESPONDING STATES ANALYSIS

In the absence of a detailed theory, one of the best methods for separating molecular orientational effects from center-of-mass translational effects involves comparison with a reference substance. This reference substance should be similar in most respects to the substance in question, but should possess no orientational degrees of freedom. Thermodynamic properties of different substances are most readily compared via a "corresponding states" analysis[5] in which all relevant thermodynamic quantities are first put in a dimensionless "reduced" form using appropriate "characteristic" quantities such as the liquid-vapor critical parameters P_c, v_c, and T_c or distance and energy parameters σ and ϵ from an intermolecular potential function. Table I gives the critical and potential parameters used for our analyses of Ar, CH_4, and N_2. (The same type of characteristic parameters must, of course, be used for each substance to be compared.) Once the data have been put in reduced form, the reduced equation of state, phase boundaries, etc., are the same for all substances which obey a "law of corresponding states." It can be rigorously shown that all classical substances for which the interparticle interactions are conformally related must obey such a law (see Ref. 5).

An ideal reference system for comparison with

TABLE I. Critical constants and potential parameters.

	N_2	CH_4	Ar
T_c (°K)	126.20[a]	190.50[b]	150.70[c]
P_c (bars)	34.0[a]	45.9[b]	48.6[c]
V_c (cm^3/mole)	89.2[a]	98.6[b]	74.9[c]
ϵ/k (°K)	95.05[d]	148.2[d]	119.8[d]
σ (Å)	3.70[d]	3.817[d]	3.405[d]
R_{nn} (Å)	4.11[e]	4.25[e]	3.86[e]

[a] R. T. Jacobsen, Ph.D. thesis (Washington State University, 1972) (unpublished).

[b] V. Jansoone, H. Gielen, J. de Boelpaep, and O. B. Verbeke, Physica 46, 213 (1970).

[c] Literature values summarized by R. K. Crawford in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, New York, to be published).

[d] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964).

[e] R_{nn} is the nearest-neighbor distance in the solid at the triple point. Values for CH_4 and N_2 are from Ref. 2, for Ar from the summary cited in note c above.

CH_4 and N_2 is the monatomic noble gas Ar. The molecules of CH_4 and N_2 interact with one another predominantly via van der Waals attractive forces and "hard" short-range repulsions, quite similar to the interactions between Ar atoms, so that approximate correspondence between the center-of-mass translational effects in CH_4, N_2, and Ar might be expected. As a first approximation, any deviations from correspondence could then be ascribed to the effects of the orientational degrees of freedom in CH_4 and N_2. [Such applications of corresponding states have been quite successful in analyzing recent inelastic neutron scattering data for fluid CH_4 (Ref. 6) and N_2 (Ref. 7).] Close correspondence is indeed observed for the fluid equation-of-state data for the three substances at points far from the freezing line,[8] and approximate correspondence between CH_4 and Ar persists through some of the solid thermodynamic data as well.[9] Figures 1 and 2 compare the reduced melting data for the three substances. The failure of CH_4 and N_2 to correspond with the melting properties of Ar is quite striking, as is the rather close correspondence found between CH_4 and N_2. These two features of the comparisons are independent of the type of parameters used in the reductions. (If triple-point fluid or solid parameters had been used in the reductions, v_f and v_s would correspond better, but Δv would not, nor would P, Δs, or Δu.)

This failure to correspond is not really surprising, especially since melting is one of the most sensitive phenomena which could be used for such a test. The CH_4 and N_2 molecules are, after all, not spherically symmetric like the Ar atoms, so their intermolecular interactions depend on the relative orientations of pairs of molecules as well as on the distance between the molecular centers. The extent and type of correlations among the molecular orientations, particularly those of near neighbors, can be expected to influence strongly the degree of overlap of the hard repulsive cores of the molecules, and so have significant effects on the energies of the fluid and solid phases. Such correlations will also affect the ways in which the molecules can be packed together in both phases.

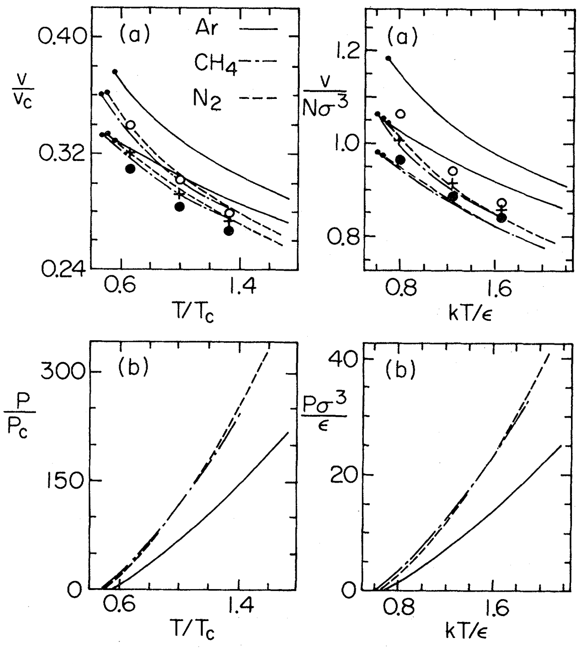

FIG. 1. Reduced melting curves for Ar, CH_4, and N_2. (a) Fluid and solid molar volumes. Calculated results from models A (open circles) and B (plus signs) of the text are also indicated. Solid circles show calculated v_s values for both models. (b) Melting pressures. All reductions are based on the parameters given in Table I.

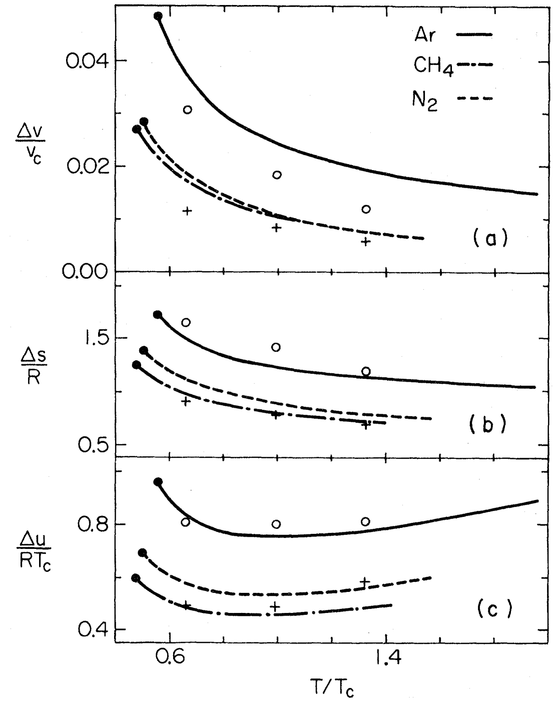

FIG. 2. Reduced melting data for Ar, CH_4, and N_2. (a) Molar volume change on melting. (b) Molar entropy change on melting. (c) Molar internal energy change on melting. Calculated results from models A (open circles) and B (plus signs) of the text are also indicated. The calculated Δs values for models A and B are based on the respective calculated v_f and v_s values and on extrapolated Ar fluid and solid entropy data (Refs. 11 and 12). Any reasonable extrapolations would give similar results. For model A the δs values from Fig. 3 are also included in the calculation of Δs. The calculated Δu values come from $\Delta u = T\Delta s - p\Delta v$, using calculated Δs and Δv results for the respective models.

Only if these orientational correlations, or "local orientational structure," were approximately the same in the fluid and solid phases would it be reasonable to expect correspondence between the melting properties of CH_4, N_2, and Ar. (Such would be the case, for example, if the CH_4 and N_2 molecules were freely rotating in both solid and fluid phases.) What is perhaps surprising, however, is the nearly complete correspondence between CH_4 and N_2, evident in Figs. 1 and 2. These two molecules have quite different shapes and even require different numbers of coordinates (three for CH_4, two for N_2) to describe their orientations. If this close correspondence is not accidental, then any explanation proposed for melting in these substances must be insensitive to such differences in the orientational symmetries (i.e., the shapes) of the individual molecules involved, beyond the requirement that the shape be nonspherical.

II. THERMODYNAMIC CONSIDERATIONS

The thermodynamic melting equations are

$$g_f = g_s ; \quad T_f = T_s ; \quad P_f = P_s , \tag{1}$$

where P, T, and g are the pressure, temperature, and molar Gibbs potentials of the solid (s) and fluid (f) phases. These simultaneous equations can be solved graphically by introducing the molar volume as an independent variable and using the Maxwell double-tangent construction[10] with the fluid and solid molar Helmholtz potentials f. Figure 3 illustrates the experimental f curves[11, 12] for Ar at 100, 150, and 200 K, with extrapolations described in the Appendix. Also shown are straight lines tangent to the solid f curves and having slopes which correspond to the melting pressures of N_2 at the corresponding temperatures. (For simplicity, this discussion refers to N_2 only. However, since N_2 and CH_4 melting properties correspond closely, everything said for N_2 will apply to CH_4 as well.) The question is now asked: How must these Ar Helmholtz potential curves be modified in order to generate melting parameters which correspond to the data for N_2?

Our original hypothesis was that differences in the reduced melting properties of N_2 and Ar are primarily due to differences in the degree of local orientational order between the fluid and solid phases of N_2. [Fundamental differences in the "softness" of repulsive potentials for CH_4, N_2, and Ar cannot account for the lack of correspondence exhibited in Figs. 1 and 2. Calculations by Hoover *et al.*[13] show that reasonable differences in "softness" (e.g., r^{-12} vs r^{-9}) are insufficient to account for melting differences of this magnitude.] Clearly, to get the higher corresponding melting pressures required for N_2, the values of f in the Ar fluid must be lowered relative to those of the solid until they are tangent to the straight lines in Fig. 3. Since the Helmholtz potential is given by $f = u - Ts$, where u and s are the molar internal energy and entropy, any change in f at constant T must be due to a change in u or s or both. If the necessary shift in Helmholtz potential is to arise from entropic effects, then an increased fluid entropy (relative to the solid entropy) is required. This can be achieved by having somewhat less orien-

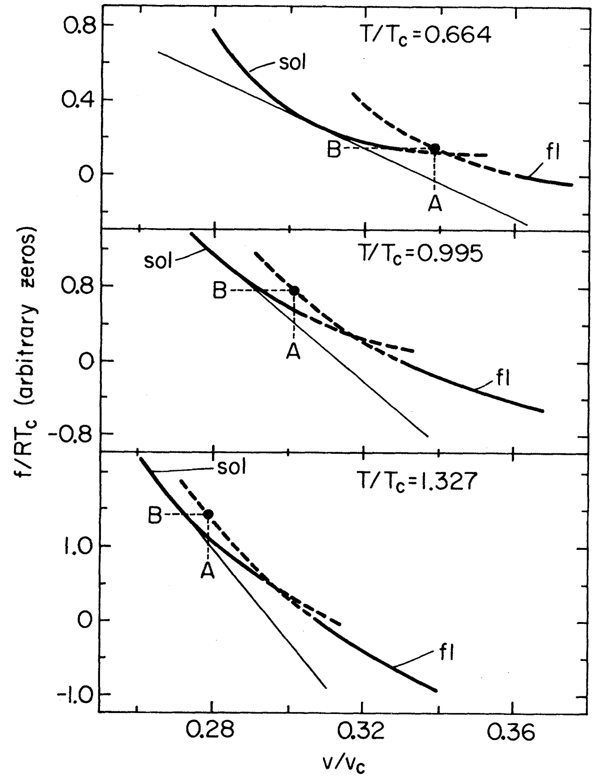

FIG. 3. Calculation of melting properties for N_2 from models A or B of the text. Curved solid lines are experimental fluid and solid Helmholtz potentials for Ar. Curved dashed lines are extrapolations based on similarities between fluid and solid experimental data (see Appendix). Straight lines tangent to solid Helmholtz potential curves have slopes giving the correct corresponding melting pressures for N_2. Closed circles indicate the points on the fluid Helmholtz-potential curves which give these pressures. Short-dashed lines indicate where these points would move if the fluid Helmholtz-potential curves were uniformly lowered (case A) or moved to the left (case B) until they were tangent to the solid straight lines. The required displacements indicated in the figure correspond to additional fluid entropies (model A) of $\delta s/R = 0.26$, 0.35, 0.29 for $T/T_c = 0.664$, 0.995, 1.327, respectively, and to fluid volumes decreased (model B) by an amount $\delta v/v_f = 0.053$, 0.030, 0.020 for the same respective temperatures.

tational correlation in the fluid than in the solid (model A). Since the "orientational" contribution to the entropy has been shown to have only a weak volume dependence,[8,9] this effect can be approximated fairly accurately by lowering the fluid f curves in Fig. 3 by constant amounts.

On the other hand, the required shift in Helmholtz potential could also arise from lowering the fluid internal energy relative to that of the solid. This could be accomplished by allowing the molecular orientations to be somewhat more ordered in the fluid than in the solid (model B). By correlating their orientations the fluid molecules could move closer together without increasing their core-overlap repulsion energy, thus taking fuller advantage of the attractive parts of the potential and producing a net lowering of the fluid energy relative to that of the solid. However, the intermolecular interactions are strong functions of the intermolecular distances, so this energy reduction should be dependent on molar volume. Looking at it another way, since increased local orientational order in the fluid allows the fluid molecules to be packed somewhat closer together than they could be otherwise, the molecules appear to have smaller effective "diameters." As a result the fluid can be represented by a correspondingly smaller characteristic volume. Thus, if energy effects are dominant, the results should be approximated by simply shifting the fluid f curves to the left in Fig. 3 (i.e., to smaller molar volumes).

The two models A and B discussed above, as represented by uniform shifts of fluid f curve *down* or to the *left,* respectively, are undoubtedly simplifications of any real physical situations. However, they probably are representative of the two competing types of behavior which are likely to give the desired N_2 melting pressures, so it is useful to discuss the consequences of these two models. Figure 3 illustrates the use of these two models to calculate the melting properties of N_2 from the experimental Helmholtz potential curves for Ar at three different temperatures. The Helmholtz potential shift is chosen to give the correct melting pressure for N_2 in each case, but the two models can be compared by looking at the predicted values for v_f, v_s, Δv, Δs, and Δu. These results are shown in Figs. 1 and 2. Both models give reduced v_f and v_s values lower than those for Ar, in agreement with the data for N_2. A more sensitive test of the two models is given by the Δv, Δs, and Δu on melting, shown in Fig. 2. The results of model B give considerably better agreement with the N_2 data than do those of model A, and some mixture of the two types of behavior could presumably give results in complete agreement with the data. In any event, the type-B behavior appears to predominate. Thus this line of rather indirect thermodynamic reasoning suggest that dense fluid N_2 has a *greater* degree of local orientational order than does solid N_2 near melting! Since N_2 and CH_4 correspond, the same conclusion is suggested for CH_4 as well.

It should be noted that an indirect argument such as that used above is necessary in any attempt to compare differences between fluid and solid N_2 with corresponding differences between fluid and solid Ar near the melting curve. One cannot, for example, directly compare the Δs and Δu values measured for N_2 with the corresponding data for Ar, because Δs and Δu not only depend on the respective $s(v, T)$ and $u(v, T)$ curves in each phase, but also depend strongly on Δv (see the discussion in Ref. 4). Since Δv on melting is quite different for N_2 than for Ar (in a corresponding-states sense), direct comparisons of Δs or Δu by themselves are meaningless.

Some additional evidence consistent with the above results can be found in the fluid and solid equation-of-state data for CH_4, N_2, and Ar. A careful analysis of the data of Refs. 8, 9, 11, and 12 shows that for Ar near the melting curve the derivative $(\partial P/\partial T)_v$ for the fluid is less than or equal to the value for the solid at the same temperature, while for N_2 and CH_4 near their respective melting curves $(\partial P/\partial T)_v$ is (10–30)% greater for the fluids than for the solids at the same temperatures. Since $(\partial P/\partial T)_v$ is thermodynamically equivalent to $(\partial s/\partial v)_T$, this means that the entropy increases faster with increasing volume in the fluid phase than it does in the solid phase for CH_4 and N_2, while this is not the case for Ar. Such behavior suggests that in dense fluid CH_4 and N_2 there is an additional source of "order" which can be eliminated by increasing v. This lends support to the above conclusion that the local orientational order in these substances may be greater in the fluid than in the solid.

III. DISCUSSION

One traditional method of investigating fluid structures is to use x-ray or neutron diffraction techniques, and by a Fourier transform obtain the radial distribution function $g(r)$.[14] Such functions are difficult to measure accurately, and typically have relatively large experimental uncertainties. Although the experimental $g(r)$ curves[15] for Ar, CH_4, and N_2 are too uncertain to permit quantitative determination of small shifts in local structure or in relative molecular diameters of the magnitudes indicated in Fig. 3, they do show that the basic distributions of molecular (or atomic) centers are similar for all three fluids. This provides further evidence of the validity of a corresponding-states treatment of the center-of-mass contributions to thermodynamic properties. Structure seen in the experimental atom-atom distribution function[15] for liquid N_2 indicates that there are indeed strong local orientational correlations in this fluid. Recent inelastic neutron scattering experiments[7] also support this conclusion.

The local structure of dense fluid Ar is relatively well understood and is similar to that for solid Ar, with approximately the same nearest-neighbor distance but with a sufficient number of missing atoms or "vacancies" to reproduce the correct density.[16] (Of course, there is no long-range order in the fluid such as that in the solid.) However, in the case of N_2 (Ref. 17) or CH_4 (Ref. 18) there are several solid phases to choose from as shown in Fig. 4, so if the respective local fluid structures were to mimic the solid structures in N_2 or CH_4, it is not obvious which solid phases would be chosen. It is known that there is long-range orientational order in both the α and γ phases of N_2, and that the β phase has long-range order with respect to one of the orientational coordinates but not the other.[19] The extent of the short-range orientational correlations in β-N_2 is unknown, however. It has also been inferred that the α phase of CH_4 has no long-range orientational order, while the β and γ phases do.[20] The volume jumps in going from α- to β-N_2, from γ- to β-N_2, and from β- to α-CH_4 are indicated in Fig. 4. These jumps are of the order of 1% in all cases. Undoubtedly, there are volume changes of comparable magnitude associated with the gradual additional loss of local orientational order as the melting curve is approached through the high-temperature solid phase for either substance. Furthermore, the relative freedom of molecular positions in the fluid compared to that in the solid might easily permit an even more favorable orientational packing with a resulting additional volume change. Considering all these factors, it does not seem unreasonable to expect that effective fluid volume decreases of (2–5)% could be accomplished by increased local orientational order in the fluid relative to the high-temperature solid phases. According to Figs. 1–3, effective fluid volume shifts in CH_4 and N_2 of just this magnitude would be sufficient to account for nearly all the differences between the melting properties of CH_4 and N_2 and those of Ar. It is also reasonable to suppose that this local orientational order might be similar to that found in the respective low-temperature phases of these substances.

In the case of CH_4 little more can be said at present, since the orientational structures of the β and γ solid phases appear to be quite complicated.[20] However, the structures of the orientationally ordered α and γ phases of solid N_2 are relatively simple, and it is tempting to speculate that the local orientational order in dense fluid N_2 closely resembles that of one of these two phases. If α-N_2-type local orientational order were the case for fluid N_2 near triple-point conditions, then the solid behavior would suggest that, as the pressure is increased along the melting curve, the fluid structure might gradually evolve until the local orientational order in the fluid resembled that of γ-N_2. The solid data would further suggest that this should occur in the pressure range ~4–8 kbars, a possibility which could be checked by x-ray or neutron structure-factor measurements over an experimentally accessible pressure range. However, it may also be the case that the local orientational order in fluid N_2 does not look like that in α- or γ-N_2, but rather like a version of β-N_2 with strong local orientational correlations, or indeed possibly like something differing from all of these.

It is recognized that these suggestions about fluid orientational order in N_2 and CH_4 are quite

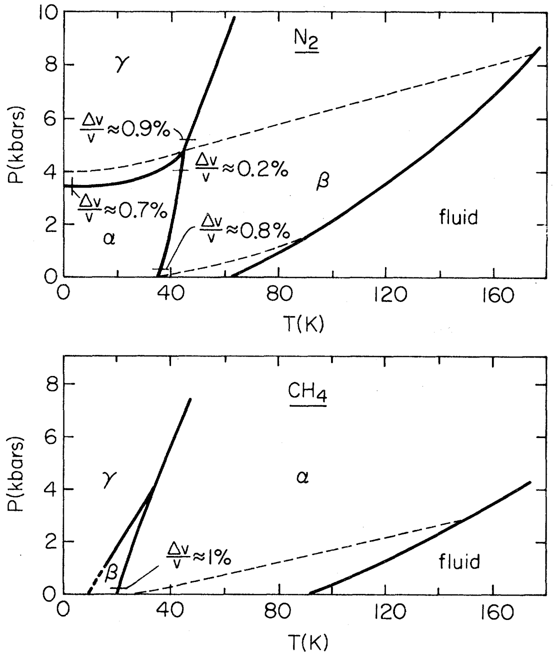

FIG. 4. Phase diagrams for solid N_2 and CH_4. Data taken from Refs. 17 and 18, respectively. The volume jumps associated with some of the low-temperature transitions are indicated. Dashed curves show selected isochores (constant-volume traces).

speculative. Nevertheless, since this idea of *increased* orientational order in the fluid is sufficient to account for nearly all the melting data in N_2 and CH_4, we feel that it is worthy of further investigation. In fact, we suggest that similar ideas might also be applicable to the entire class of materials which lose at least part of their orientational order in the solid phase before melting.[1] Direct experimental tests which could resolve these small differences in local orientational correlations appear quite difficult. Indeed, it is only because of the extreme sensitivity of melting behavior to small changes in fluid or solid properties that the molecular orientations exhibit such easily observable effects on the N_2 and CH_4 melting data. It may be that the differences in the various local structures will prove to be greater than the uncertainties inherent in x-ray or neutron local structure determinations. It is also likely that transport properties, such as the self-diffusion coefficient, or various other dynamical properties will be particularly sensitive to the local orientational correlations in fluid and solid (cf. Ref. 7). Careful analyses of such data may provide much additional information about such orientational effects.

It is also probable that greater light can be shed on this subject of local molecular orientational correlations by Monte Carlo or molecular dynamics calculations, which have long been useful in elucidating structures in monatomic systems and which are now being applied to potentials which can simulate simple molecules such as N_2.[21] Calculations which could verify or refute the present suggestions concerning the orientational correlations in systems of nonspherical molecules are not yet available; however, recent molecular dynamics calculations on a rough-sphere system indicate that *rotational motions* can exhibit a greater degree of correlation in the fluid than in the solid near melting.[22] It is hoped that the arguments presented here will stimulate further calculations of this type.

APPENDIX

It is well known that fluid argon near the melting curve has a local "structure" approximately like that of the solid near the melting curve at the same temperature, with fluid and solid having essentially the same nearest-neighbor distance.[16] Higher-order volume derivatives of the Helmholtz potential are most sensitive to nearest-neighbor distance and to the number of nearest neighbors, so it is reasonable to assume that the derivative $(\partial^2 f_f/\partial v_f^2)_T$ evaluated at v_f depends only on the nearest-neighbor distance and so is approximately equal to $\gamma(\partial^2 f_s/\partial v_s^2)_T$ evaluated at $v_s' = \beta v_f$, where γ and β are constants. When this equation is integrated, one obtains

$$f_f(v_f) - f_f(v_{fm}) + P_m(v_f - v_{fm}) = \beta^2\gamma[f_s(v_s') - f_s(v_{sm}) + P_m(v_s' - v_{sm})] , \tag{A1}$$

where v_{fm} and v_{sm} are the fluid and solid molar volumes at melting at temperature T. The constant β is chosen to make the fluid at molar volume v_f have the same nearest-neighbor distance as the solid at molar volume v_s', so a good approximation is $\beta = v_{sm}/v_{fm}$.

The experimental equation of state for the solid phase of Ar has a particularly simple form which can readily be extrapolated beyond the melting curve.[12] Comparison of the resulting extrapolated solid f curves with the experimental fluid f curves yields a value of $\gamma = 0.96$ and shows excellent agreement with Eq. (A1). One can thus be confident that the fluid f curves can reasonably be extrapolated to volumes less than v_{fm} by using Eq. (A1) and the experimental solid f curve. If a similar relationship between other volume derivatives of f had been assumed (e.g., $\partial^3 f/\partial v^3$), the resulting extrapolations would not have been significantly different over the range of interest for Fig. 3.

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[20] See, for example, H. M. James and T. A. Keenan, J. Chem. Phys. 31, 12 (1959), and references contained therein. Recent neutron scattering experiments on solid CD_4 [W. Press, J. Chem. Phys. 56, 2597 (1972)] indicate no long-range and little short-range orientational order in the α phase, while the β and γ phases have long-range orientational order for most of the molecules. The structures of the β and γ phases of CH_4 will probably be similar, if not identical, to the relatively complicated orientational structure found for CD_4, while the α phases of both materials are likely to have similar orientational disorder.

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