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MELTING CURVE AT HIGH PRESSURE*

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The temperature in the interior of the earth could be determined with greater certainty if the melting point, particularly of iron, were known under the pressure conditions of a few megabars existing there. Although experiments with shocks could determine the melting curve up to these pressures, they appear to be difficult to carry out in practice. It has therefore been necessary to rely on a long extrapolation, by an empirical equation, of static melting data, since these have reached only about $\frac{1}{10}$ of the desired pressure. A more reliable alternative, explored in this note, is to use computer experiments to investigate melting at a few megabars. In this way the accuracy of the postulated Lindemann law[1] and Simon equation[2] for extrapolation purposes can be investigated.

The computer experiments by the so-called Monte Carlo method[3] have as their only limitations that the intermolecular potential must be pair-wise additive, that the runs must be sufficiently long to sample all of the important configurations, and that the restrictions of dealing with only a few particles (108 in the present study) does not seriously distort the results. The importance of the last two limitations was investigated by comparing the computer results with experimentally observed melting conditions for argon, a system where the potential is known, at least at low pressures, to be very close to pair-wise additive. The potential used was consistent with a statistical mechanical analysis of the available thermodynamic properties of argon, particularly for solid[4] and gaseous[5] argon where this analysis can be carried out analytically. The potential at small interatomic distances, required for the description of high-pressure behavior, was similarly deduced from a Monte Carlo computer analysis[6] of the thermodynamic data obtained by the use of explosively generated shocks.[7] This analysis, consistent with the pair-wise additivity assumption, showed the potential to be in good agreement with molecular beam experiments[8] as well as with theoretical calculations of the pair potential on the basis of the Thomas-Fermi-Dirac model.[9]

With this intermolecular potential and 108 particles placed initially in a face-centered cubic lattice with periodic boundary conditions, the melting behavior was studied at three temperatures. The comparison with experiment[4] at 1010 bars is given in Fig. 1. All the data are summarized in Table I. The type of melting discontinuity shown in Fig. 1 is typical of the distortion of the flat region of the isotherm observed in large systems. In small systems the fluid and solid phase cannot coexist, hence the system at a given density jumps back and forth between the two phases.[10] The correct choice of the intermolecular potential is indicated by the close agreement of the isotherm with experiments outside the two-phase region. If the tie line is drawn at the highest fluid density at which the transition to the fluid phase from the initial solid phase can be observed, then the agreement of the pressure and the coexisting solid and liquid volumes with experiment is very good indeed. The method can therefore be trusted to give an accurate melting temperature even at high pressures, provided the pair-potential approximation does not break

Table I. Comparison of the Monte Carlo results with empirical melting equations.

Monte Carlo results			Simon		Lindemann	
T_m (°K)	P_m (kbar)	V_s (cc/mole)	P_m [a]	P_m [b]	θ (°K)	b
83.81[c]	0.00	24.61	0.00	0.00	46.72	93.80
108.15	1.01 ± 0.08	24.40 ± 0.12	1.05	1.05	48.02	84.64
2440	292 ± 10	11.44 ± 0.12	353	452	274.4	79.09
12 200	3970 ± 30	5.815 ± 0.015	3970	5898	790.4	81.33

[a]Ref. 13. [b]Ref. 14. [c]Experimental data.

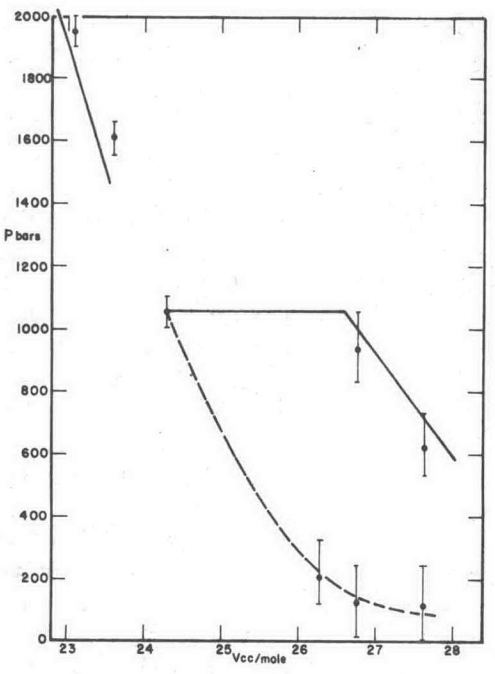


FIG. 1. Comparison of the experimental 108.15°K isotherm of argon (solid curve) in the neighborhood of the melting transition with Monte Carlo results (circles). The vertical bars indicate the statistical accuracy of the results. The experimental isotherm is drawn only where data are available, hence the incomplete curve on the solid side close to melting. The dashed curve represents the metastable solid branch generated by the Monte Carlo results.

down.

It is unlikely that pair-wise additivity is valid at the highest melting point given. Argon has been observed to have metalliclike conduction under less severe conditions.[7] Thus, at worst, the melting curve, but only at the extreme conditions, has to be considered as that of a hypothetical substance on which accurate experiments were performed on the computer. It can, however, be argued that the melting point for any substance is primarily determined by the short-range potential so that the computer experiment would still be realistic even for substances that are not insulators. The argument depends basically on the observation that even in a metal the long-range order of the ionic cores is destroyed upon melting while the electron distribution is only slightly different. More concretely, Lindemann's law is able to predict melting conditions under atmospheric conditions for both metals and insulators on the same physical basis.

Lindemann's law states that a substance melts once a particle can, with high probability, make an excursion from its regular lattice site through about 10% of the intermolecular distance. The melting of hard spheres and disks conforms to this rule very closely.[11] The rule can be restated in terms of more directly measurable quantities as

$$(\theta^2 V_m^{2/3} M/T_m)^{1/2} = b,$$

where θ is the Einstein temperature, V_m is the melting volume of the solid, T_m is the melting temperature, and M is the molecular weight. The constant b is universal and depends only on the crystal structure. The Einstein θ, in the spirit of Lindemann's model, is calculated from the harmonic-oscillator frequency determined by the Taylor expansion of the total interaction potential of an atom with the remainder of the lattice. The great accuracy of Lindemann's law as applied to argon, in spite of an over 100-fold range in melting temperature and a four-fold decrease in volume, is seen in Table I. These large ranges are compensated for by the increase in order of magnitude of the Einstein temperature. Not only is b nearly constant over this enormous range, but its absolute magnitude conforms closely to the rule for amplitude of oscillation previously found valid for many metals, insulators, and the hard sphere system. Thus Lindemann's law is able to predict the entire melting curve without normalization to any given melting conditions. Its universal validity depends on the predominance of the repulsive forces in determining melting, and these forces are similar in character for all real systems. The repulsive forces are particularly dominant at high pressure and thus Lindemann's law should be even more accurate there. This is confirmed by the data given in Table I.

These observations are to be contrasted with an empirical relationship recently reported in which the melting temperature varies linearly with compression.[12] This empirical relation makes the unlikely prediction that at infinite compression the melting temperature of potassium, for example, would be 604°C. The data given in Table I indicate that the melting temperature varies exponentially with compression, therefore the linear relation is valid only for small compressions and should not be used for extrapolation to the large compressions that exist, for example, in the interior of the earth.

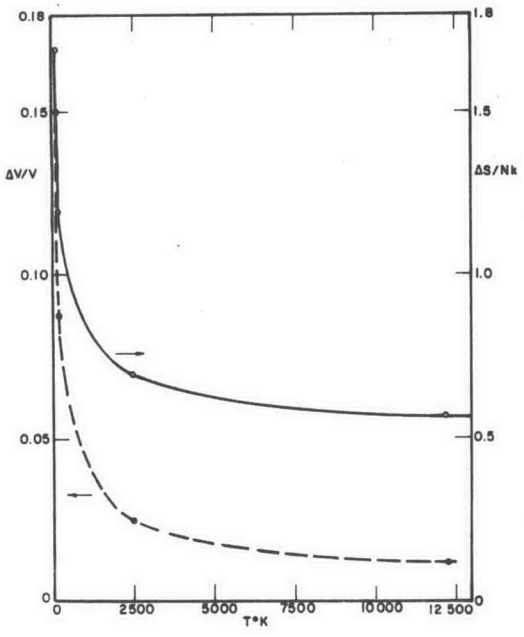


FIG. 2. The relative volume (dashed curve) and entropy change (solid curve) upon melting as a function of the melting temperature.

The accuracy of Simon's equation[2]

$$P_m = a[(T_m/T_0)^c - 1]$$

is also illustrated in Table I. T_0 is the triple point of argon. The constants a and c are both determined from a fit to the melting data at low pressure.[13,14] The results given in Table I show that the large extrapolation to high pressure is exceedingly sensitive to the fit at low pressures.

Finally, the Monte Carlo data indicate the absence of a solid-fluid critical point. Figure 2 shows that the volume and entropy changes upon melting approach an asymptotic limit at high pressures. These and further details will be published elsewhere.

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