Thermochimica Acta, 179 (1991) 333–336
Elsevier Science Publishers B.V., Amsterdam

Note

A SIMPLE COMPUTER APPROACH FOR DETERMINING MELTING POINTS [a]

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(Received 27 July 1990)

ABSTRACT

Melting points are critical to the study of material changes of state. The concept of a melting point is formulated here in terms of only four atoms or molecules. Computer implementation results in a general formula which is applied to solids which consist of a single atomic or molecular species. This new formula is in terms of Planck's constant.

The melting point of a solid is usually defined in terms of the average kinetic energy of a large ensemble of atoms or molecules [1]. We explore here a new computer-oriented model of the melting point which uses only four atoms or molecules.

Consider first four identical atoms P_1, P_2, P_3, P_4, each of mass m. Let $\phi(r)$ be a related classical interatomic potential and let F be the interatomic force defined by ϕ. Let F be zero when r equals r^*, which is called the equilibrium distance. Although r and r^* will be given in ångströms, all other quantities will be given in cgs units.

Next set P_i $(i = 1, 2, 3, 4)$ to be the vertices of a regular tetrahedron of edge length r^*, at the respective points (x_i, y_i, z_i), as shown in Fig. 1, in which, for convenience, $(x_1, y_1, z_1) = (0, 0, [(r^*)^2 - (\frac{2}{3}r^* \sin 60°)^2]^{1/2})$ $(x_2, y_2, z_2) = (0, \frac{2}{3}r^* \sin 60°, 0)$ $(x_3, y_3, z_3) = (\frac{1}{2}r^*, -\frac{1}{3}r^* \sin 60°, 0)$ $(x_4, y_4, z_4) = (-\frac{1}{2}r^*, -\frac{1}{3}r^* \sin 60°, 0)$.

For this arrangement, P_2, P_3, and P_4 are in the XY plane and are equidistant from the origin, while P_1 lies on the Z axis.

To derive a formula for the melting point of a solid, we begin by studying, in particular, copper. For this purpose, note first that a Lennard-Jones (6–12) potential for copper is [2]

$$\phi(r) = -\left(\frac{1.398}{r^6}\right)10^{-10} + \left(\frac{1.551}{r^{12}}\right)10^{-8} \qquad \text{(erg)} \tag{1}$$

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[a] Calculations were performed on the CRAY X-MP/24 at the University of Texas Center for High Performance Computing.

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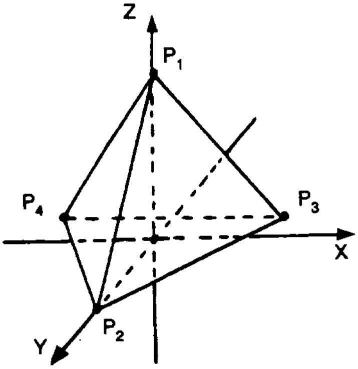

Fig. 1.

In dynes, the force $\boldsymbol{F}$ then has magnitude F given by

$$F = -\frac{(8.388)}{r^7}10^{-2} + \left(\frac{18.612}{r^{13}}\right) \tag{2}$$

from which it follows that $r^* = 2.460$ Å. We now apply molecular dynamics to the tetrahedral system P_1, P_2, P_3, P_4. The initial velocities are chosen to be $\boldsymbol{V}_1 = (\mathbf{0}, \mathbf{0}, V_z)$, $\boldsymbol{V}_2 = \boldsymbol{V}_3 = \boldsymbol{V}_4 = 0$, and we determine numerically the minimum value of V_z for which P_1 passes through the plane of P_2, P_3, P_4. Intuitively, such behavior is fluid-like and should enable one to characterize the melting transition. The result is $V_z = 0.20356 \times 10^{-15}$ cm s^{-1}. If v_1 is the initial speed of P_1 relative to the center of mass of the system [3], so that $v_1 = \frac{3}{4}V_z$, then $v_1 = 0.15267 \times 10^{-15}$ cm s^{-1}. We now define the melting point T_0 of copper in K by the formula

$$T_0 = C\left(\tfrac{1}{2}mv_1^2\right) \tag{3}$$

in which C is a constant which is determined as follows. Since the mass of a copper atom is 1.0542×10^{-22} g and its melting point is $T_0 = 1357$ K, eqn. (3) implies

$$C = 1.10453 \times 10^{-57} \tag{4}$$

But, to 0.03%, which is less than the error in the experimental value 1357 K, one finds

$$C = \left(\frac{h}{6}\right) \times 10^{84} \tag{5}$$

in which h is Planck's constant 6.6251×10^{-27} J s.

From the results above, we now propose that the melting point for any system P_1, P_2, P_3, P_4 is

$$T_0 = \left(\frac{h}{6}\right) \times 10^{84}\left(\tfrac{1}{2}mv_1^2\right) \tag{6}$$

TABLE 1

Noble gas	ϵ ($\times 10^{-16}$ erg)	σ (Å)	r^* (Å)	Mass ($\times 10^{-24}$ g)	V_z ($\times 10^{-15}$ cm s^{-1})	Melting point (K)	T_0 (K)
Ne	48.1837	2.78	3.12044	33.49754	0.04763	24	24
Ar	168.436	3.40	3.81637	66.31447	0.06292	84	82
Kr	236.086	3.60	4.04086	139.10966	0.05251	116	119
Xe	299.595	3.963	4.44832	217.96061	0.04872	161	161

and proceed to examine the applicability of this formula to other atomic species.

In Table 1 we have listed the parameter values for the Lennard-Jones potentials

$$\phi(r) = 4\epsilon\left[-\left(\frac{\sigma}{r}\right)^6 + \left(\frac{\sigma}{r}\right)^{12}\right] \tag{7}$$

for the noble gases Ne, Ar, Kr and Xe. These potentials were derived using second virial coefficients [4]. Also listed are the respective masses, equilibrium distances r^* and minimum values V_z determined by molecular dynamics. The experimental melting points and the theoretical values determined using eqn. (6) are given in the final two columns. The agreement is quite good.

We finally turn to molecular species, for which many more potentials are available than for atomic species. For simplicity, we will restrict attention to potentials of the form of eqn. (7) for which at least three different sets of parameter values are available. From table I-A of Hirschfelder, Curtiss and Bird [5], then, attention will be directed to N_2, O_2, CO, NO and CH_4. Again using molecular dynamics, the appropriate tetrahedral structures and eqn. (6), we obtain the results listed in Table 2. In the first column, an entry without an asterisk is one which has been determined using the second virial coefficient, while one with an asterisk has been determined by means of viscosity. The parameter values for any particular molecule can vary quite extensively, as is readily observed for NO. The computational results are summarized as follows.

For N_2, the choice $\epsilon/k = 95.05$, $\sigma = 3.698$ is best. The result of 63.9 K is in error by 0.16%. However, all the results are narrowly within the correct range. Indeed, for the worst case (corresponding to $\epsilon/k = 79.8$, $\sigma = 3.749$) the computed result is in error by only 0.78%. For CO, the choice $\epsilon/k = 110$, $\sigma = 3.590$ is best and yields an error of 1.6%, while for CH_4 the choice $\epsilon/k = 144$, $\sigma = 3.796$ proves best and the error is 1.2%.

The remaining two cases O_2 and NO, require special attention. Although for O_2 the choice $\epsilon/k = 88.0$, $\sigma = 3.541$ is better than the other three possibilities, it yields an error of 19.7%. We then assumed an error of 5% in both ϵ/k and σ and re-ran all possible resulting cases. For the 5% variations

TABLE 2

Molecule	ϵ/k (K)	σ (Å)	Mass ($\times 10^{-24}$ g)	V_z ($\times 10^{-15}$ cm s^{-1})	Melting point (K)	T_0 (K)
N_2 (a)	95.9	3.71	46.5028	0.06676	64	64.4
(b)	95.05	3.698		0.06650		63.9
(c) *	91.5	3.681		0.06645		63.8
(d) *	79.8	3.749		0.06681		64.5
O_2 (a)	118.0	3.46	53.5	0.06855	54.6	78.1
(b)	117.5	3.58		0.06857		78.1
(c) *	113.0	3.433		0.06715		74.9
(d) *	88.0	3.541		0.05992		59.6
CO (a) *	110.0	3.590	46.6887	0.07087	74	72.8
(b)	100.2	3.763		0.06819		67.4
(c) *	88.0	3.706		0.06403		59.4
NO (a)	131.0	3.17	50.0014	0.07394	109	84.9
(b) *	119.0	3.470		0.07105		78.4
(c) *	91.0	3.599		0.06287		61.4
CH_4 (a)	148.2	3.817	26.6319	0.1093	90.5	98.8
(b) *	144.0	3.796		0.10525		91.6
(c) *	137.0	3.822		0.1030		87.7

See text for the meaning of the asterisk.

($\epsilon/k = 83.6$, $\sigma = 3.71805$) there resulted $V_z = 0.05875$ cm s^{-1}, $T_0 = 57.3$ K, which is in error also by just under 5%. This was the best of all of the results. A possible problem which may be apparent from this example is that the approximation of F by differentiation of ϕ leads to an inordinate increase in the error in ϕ. Unfortunately, unlike integration, differentiation can exhibit such a property.

For NO, the values $\epsilon/k = 131$, $\sigma = 3.17$ are best, but the results are still quite poor. Even use of the 5% error idea which was applied to O_2 yielded at best $V_z = 0.07587$ cm s^{-1}, $T_0 = 89.4$ K for $\epsilon/k = 137.55$, $\sigma = 3.3285$. Therefore, either the problems inherent in differentiation are present, or the Lennard-Jones potential is not applicable, or eqn. (6) is no longer valid.

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