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A SIMPLE METHOD FOR THE CALCULATION OF THE EQUATION OF STATE

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A SIMPLE METHOD FOR THE CALCULATION OF THE EQUATION OF STATE

I. The calculation of the equation of state at high temperature is usually done by the evaluation of integrals of the type $e^{-u/kt}$, where u is the potential energy of one particle. If the potential energy is complicated, the calculations are very tedious, and considerable approximations have to be made. This paper proposes an exceedingly simple method for the calculation of the equation of state. Its validity is going to be tested by comparison with available data for Argon, and with the extensive calculations for this substance made by the standard methods.*

II. The method consists in calculating the entropy of the substance at constant energy. If we assume the substance to be monatomic (inclusion of rotation and vibration present no difficulty), the energy is the sum of potential and kinetic energy,

$$E = E_K + E_p \quad .$$

At high density, it will be assumed that the atoms are approximately close packed, so that each atom has 12 nearest neighbors, at distance R from the equilibrium position of the atom. The potential of the nearest neighbors is calculated as if the particles were smeared out evenly over a sphere of radius R. If the particle is at a distance $d < R$ displaced from its equilibrium position, the potential u acting on it is

$$u(d, R) = \frac{6}{Rd} \int_{R-d}^{R+d} y \, V(y) \, dy \qquad (1)$$

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* R. J. Buehler, R. H. Wentorf, J. O. Hirschfelder and Charles F. Curtiss

The total energy can then be approximated as

$$E = E_K + \sum_{i=1}^{N} \left[u(d_i, R) - u(0,R) \right] + \frac{N}{2} u_0(0)$$

$$= E_K + \sum_{i=1}^{N} u(d_i, R) - \frac{N}{2} u_0(0,R)$$

Since the energy is assumed to be constant, an appropriate average value of d can be found such that

$$E = E_K + N(u(d,R) - \frac{1}{2} u(o,R) = E_K + N\epsilon \qquad (2)$$

where

$$\epsilon(d,R) = u(d,R) - \frac{1}{2} u(o,R). \qquad (3)$$

The entropy is the total phase volume below the energy E. For its calculation, the essential, and doubtful, assumption is made that all atoms have actually the same energy. The configuration volume available for each particle is then $\frac{4\pi}{3} d^3$, and the entropy becomes, leaving out all constant terms,

$$S = \frac{3}{2} N k \ln E_K + 3 N k \ln d. \qquad (4)$$

The assumption made of equal energy, and consequently equal free volume per particle is probably not quite as bad as it seems at first sight. In the case of simple harmonic motion, for instance, it introduces no error at all. In that case, $d = a\sqrt{E_{p/N}}$; the correct method would consist in forming the volume of the 3N dimensional sphere with radius $a\sqrt{E_p}$. Since this volume is proportional to d^{3N}, with a proportionality factor depending on N only, it is seen that the correct expression for S differs from (4) only by a constant additive term, which disappears in differentiation. In general, it is claimed in (3) only that the available configuration volume is proportional to d^{3N} with a constant proportionality factor.

III. From here on the calculation is straightforward. The division of energy into kinetic and potential has to be made such that S is a maximum.

$$0 = \frac{\partial S}{\partial E_K} = \frac{3}{2}\frac{Nk}{E_K} - \frac{3k}{d}\left[\frac{\partial d}{\partial \epsilon}\right]_R \tag{5}$$

The derivative of the entropy with respect to the energy is

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3Nk}{2E_K}\frac{\partial E_K}{\partial E} + \frac{3k}{d}\frac{\partial d}{\partial \epsilon}\frac{\partial N\epsilon}{\partial E} \tag{6}$$

Combination of these equations leads to

$$E_K = \frac{3}{2}NkT, \tag{7}$$

$$d\left(\frac{\partial \epsilon}{\partial d}\right) = 3kT. \tag{8}$$

The equation for the pressure is obtained by differentiation of S with respect to V

$$\frac{P}{T} = \frac{\partial S}{\partial V} = \frac{R}{3V}\frac{\partial S}{\partial R} = \frac{RNk}{Vd}\left(\frac{\partial d}{\partial R}\right)_\epsilon \tag{9}$$

or

$$\frac{PV}{NkT} = -\frac{R}{d}\,\frac{\partial \epsilon/\partial R}{\partial \epsilon/\partial d} \tag{9'}$$

or with the use of (7)

$$PV = -\frac{N}{3}R\,\partial\epsilon/\partial R \tag{9''}$$

The latter equation could also have been derived from the relation $P = -\left(\frac{\partial E}{\partial V}\right)_S$. Equation (9) shows that in the case of the ideal gas, where R = d, the correct expression is obtained.

Because of theform of E (eq. (1) and (3)), equations (7) and (9') can be spelled out in more detail

$$3kT = d\frac{\partial u}{\partial d} = -u + \frac{6}{R}\left[(R+d)v(R+d) + (R-d)v(R-d)\right] \tag{10}$$

$$PV = \frac{N}{3}u + \frac{2N}{d}\left\{(R-d)v(R-d) - (R+d)v(R+d)\right\} + 2NR\left(\frac{\partial v}{\partial R}\right)_{d=0} \tag{11}$$

$$V = NR^3/\sqrt{2} \tag{12}$$

Thus, by picking a value of R, which determines the volume, and a value of d, it is easy to calculate T, P and E.

IV. There is one improvement which can be applied to this method without much added complication, and which should improve the results, especially at lower density. The assumed crystaline structure of 12 nearest neighbors is certainly incorrect at low densities. One can take care of this, to some extent, by assuming the existence of "holes". It shall be assumed that there exist $C > N$ "cells" in the crystal, of which only N are occupied. The ratio of particles to places, N/C, shall be denoted by W

$$N/C = W \; . \tag{13}$$

At given R and d, the potential energy is changed by the fact that now each of the N atoms has in the average only W neighbors. If their effect is again considered as smeared out over a spherical shell, the energy becomes

$$E = E_K + N\,W\,\epsilon\,(d,R) \; . \tag{14}$$

The entropy has an additive term $k \ln \frac{C!}{N!\,(C-N)!}$, and becomes

$$S = \frac{3}{2} N k \ln E_K + 3 N k \ln d - N k \left\{ \frac{W-1}{W} \ln (1-W) + \ln W \right\} \tag{15}$$

$\times \frac{1-W}{W}$

W is to be determined by maximizing the entropy. At given R and d, P, V, T and E shall stand for the results obtained from the calculations of the previous section. The corrected values shall be denoted by an asterisk. The change consists in the following :

$$\left.\begin{aligned} V^* &= \frac{1}{W} V \\ E_p{}^* &= W E_p \\ T^* &= W T \\ E^* &= W E \\ \frac{P^*V^*}{NkT^*} &= \frac{PV}{NkT} \\ P^* &= W^2 P \end{aligned}\right\} \quad (16)$$

The equation for the determination of W becomes

$$0 = \left(\frac{\partial s}{\partial W}\right)_{E,V} = \frac{Nk}{W^2} \ln(1-W) + \frac{3Nk}{d}\left[\left(\frac{\partial d}{\partial R}\right)\left(\frac{\partial R}{\partial W}\right)_V + \frac{\partial d}{\partial \epsilon_p}\left(\frac{\partial \epsilon_p}{\partial W}\right)_E\right]$$

$$= \frac{Nk}{W^2} \ln(1-W) + \frac{NkR}{dW}\left(\frac{\partial d}{\partial R}\right)_{E_p} - \frac{3Nk\epsilon_p}{3kT^*} .$$

This results in

$$-\frac{1}{W} \ln(1-W) = \frac{PV - E_p}{NkT} = \frac{P^*V^* - E_p{}^*}{NkT^*} \quad (17)$$

V. It was suggested by J. Kirkwood that this method be compared with that of assuming a square well distribution function of radius d for an atom within its cell. In this case, the potential energy per particle will be

$$\bar{\epsilon} = \frac{3}{d^3}\int_0^d x^2 \, \epsilon(x) \, dx .$$

The entropy becomes

$$S = \frac{3}{2} Nk \ln E_K - Nk\int_0^d p(x) \ln p(x) \, dx$$

$$= \frac{3}{2} Nk \ln E_K + 3Nk \ln d + \text{constant} .$$

The ensuing results are formally exactly the same, except that $\bar{\epsilon}$, or $\bar{u}$ replaces ϵ or u respectively. Using expression (1) for u

$$u = \frac{6}{Rd}\int_{R-d}^{R+d} y \, V(y) \, dy$$

one obtains for $\bar{u}$

$$\bar{u} = \frac{3}{r^3}\int_0^r x \, u(x) \, dx = \frac{9}{r^3 R}\int_{R-d}^{R+d} y \, V(y)\left[r^2 - (y-R)^2\right] dy$$

The average value of the expression in the square bracket above is $2/3\ r^2$. If the square bracket is replaced by its average value, one obtains the same expression for $\overline{u}$ as for u. It is seen that this approach would not give vastly different results. In fact, the assumption for the entropy made at the beginning of this paper (4) is consistent with any distribution function $p(x)$ for which $-\int p(x) \ln p(x)\ x^2\,dx$ is equal to a constant plus $\ln d^3$, where d is defined by $\int p(x)\ u(x)\ dx = u(d)$.