

and extend to about 70 kb. They are compared with the calculated curves in Fig. 4. In order to see what changes in the potential would have to be made to give a calculated curve through these points, we took as a starting point the second-virial-coefficient exp-six potential, Eq. (3.1). An increase of r^* to 4.18 Å at constant α and ϵ^*/k was required to match the experimental data; these values gave curve 4 of Fig. 3. An increase of ϵ^*/k to 240 °K at constant α and r^* gave a calculated curve which would be nearly indistinguishable from curve 4 if plotted in Fig. 3. It seems unlikely that the assumption of additivity of pair forces could fail so badly at these low pressures as to require such a major adjustment of the pair potential in order to match the experimental data. For this reason, and because data at higher pressures would be of considerable interest, similar experiments carried to higher pressures would be desirable.

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APPENDIX

In working with an equation of state based on a pair potential $u(r)$, it is desirable to have the energy expressed in the form

$$E = \int_0^\infty u(r)h(r) dr, \quad (A1)$$

so that the function $h(r)$ gives immediately the relative importance of different intermolecular distances.

The cell integrals of the LJD equation of state can be transformed into this form. The expressions for internal energy and pressure can be written (for nearest-neighbor interactions)

$$PV - RT = -N[\frac{1}{2}Zt f'(t) - g(\frac{1}{2}t\omega_1)/g(1)] \quad (A2a)$$

$$E' = N[\frac{1}{2}Zf(t) = g(\omega)/g(1)], \quad (A2b)$$

where Z is the coordination number, $t = a/r^*$ with a the nearest-neighbor distance, the prime denotes differentiation, and the subscript t denotes partial differentiation with respect to t . The pair potential has been written with a reduced argument: $f(r/r^*) = u(r)$. The cell potential ω is defined by

$$\omega(x, t) = \frac{Z}{2x} \int_{1-x}^{1+x} x' [f(tx') - f(t)] dx', \quad (A3)$$

and the g function by the cell integral

$$g(z) = 2 \int_0^b [z] x^2 e^{-\omega(x, t)/kT} dx, \quad (A4)$$

where b is the cell radius in units of a .

By defining $\varphi(x, t) = \exp[-\omega(x, t)/kT]$, and making use of Eq. (A3), the cell integral for the energy becomes

$$g(\omega) = Z \int_0^b dx \int_{1-x}^{1+x} dx' x \varphi(x, t) x' [f(tx') - f(t)]. \quad (A5)$$

Reversal of the order of integration gives

$$g(\omega) = Z \int_{1-b}^{1+b} dx' \int_{|1-x'|}^b dx x' [f(tx') - f(t)] x \varphi(x, t), \quad (A6)$$

or

$$g(\omega) = Z \left\{ \int_{1-b}^{1+b} f(tx') G(x', t) dx' - f(t) \int_{1-b}^{1+b} G(x', t) dx' \right\}, \quad (A7)$$

where

$$G(x', t) = x' \int_{|1-x'|}^b x \varphi(x, t) dx. \quad (A8)$$

It is easy to show that

$$\int_{1-b}^{1+b} G(x', t) dx' = g(1), \quad (A9)$$

and we thus obtain from Eq. (A2b)

$$E' = NZ \left[-\frac{f(t)}{2} + \int_{1-b}^{1+b} f(tx') \frac{G(x', t)}{g(1)} dx' \right]. \quad (A10)$$

The corresponding expression for the pressure is obtained in similar fashion,

$$PV - RT = -NZ \left[\frac{1}{2} t f'(t) - \int_{1-b}^{1+b} \frac{1}{2} t x' f'(tx') \frac{G(x', t)}{g(1)} dx' \right]. \quad (A11)$$

It is convenient to express the desired weighting function in a form analogous to the radial distribution function:

$$h(r) = \frac{Z}{2\pi \sqrt{2x'^2}} \left[\frac{G(x', t)}{g(1)} - \frac{1}{2} \delta(x' - 1) \right]; \quad x' = r/a \quad (A12)$$

with $G(x', t) = 0$ for $x' < 1 - b$ and $x' > 1 + b$, and δ the Dirac δ -function. If $h(r)$ is used instead of $g(r)$ in the usual statistical mechanical expressions for the energy and pressure, Eqs. (4.1), the results are just the LJD expressions for pressure and energy, Eqs. (A2).