

I. PHYSICS

Chemical Physics

PAIR POTENTIAL OF LIQUID NEON FROM STRUCTURE FACTOR DATA

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A method of evaluating pair-potential from experimental or theoretically evaluated structure factor data has been developed. This has been applied further to evaluate the pair-potential of liquid neon using experimental data of de Graaf and Mozer (1971). Results of calculations are good.

Keywords: Pair-potential function, structure factor, liquid neon, pressure equation of state, compressibility equation of state, direct correlation function.

INTRODUCTION

RECENTLY, much interest has been devoted to the evaluation of pair potential from the radial distribution function (Johnson *et al.*, 1964; and Brennan *et al.*, 1974). In the present paper, a method of evaluating potential function from static structure factor data will be developed and the same will be applied to liquid Neon. The method depends upon the fact that an exact theory of radial distribution function (RDF) must produce the same result from the pressure and compressibility equations of state provided the additivity of the potential holds good.

THEORY

The pressure equation of state (Hill, 1956) can be written as

$$P = \rho K_B T - \rho^2/6 \cdot \int_{\mathbf{v}} r \frac{dU(r)}{dr} g(r) d\vec{r} \quad \dots(1)$$

For small changes of pressure, one can expand the radial distribution function, $g(r)$ at the equilibrium value $g_0(r)$ at ρ_0 and write :

$$P = \rho K_B T - \rho^2/6 \cdot \int_{\mathbf{v}} \frac{dU(r)}{dr} \cdot \left[g_0(r) + (\rho - \rho_0) \times \left(\frac{\partial g(r)}{\partial \rho} \right)_{\rho_0} + \dots \right] r d\vec{r} \quad \dots(2)$$

Compressibility equation of state (Hill, 1956) may be written as :

$$- V^2/NK_B T \cdot \left(\frac{\partial P}{\partial V} \right)_T = 1 - N/V \cdot \int_{\mathbf{v}} C(r) d\vec{r} \quad \dots(3)$$

Since the direct correlation function (DCF), $C(r)$ is equal to zero at large r , but is not equal to zero at $r = 0$, one may write :

$$V^2/NK_B T. \left(\frac{\partial P}{\partial V} \right)_T = 1 + \frac{N}{3V} \int_{\mathbf{v}} C'(r) r d\vec{r} \quad \dots(4)$$

At constant temperature, eqn. (4) yields

$$P = \rho K_B T + \rho^2 K_B T/6. \int_{\mathbf{v}} r C'(r) d\vec{r} - \rho^3 K_B T/6. \int_{\mathbf{v}} \frac{\partial C'(r)}{\partial \rho} \cdot r d\vec{r} \quad \dots(5)$$

Molecules near the walls of the container have been neglected in the above derivation. Since the pressure calculated from eqns. (2) and (5) should be self-consistent, one can equate the co-efficients of ρ^2 in the above two equations, neglecting terms involving cubes or higher powers of ρ since they involve very small quantities like $(\rho - \rho_0) (\partial g(r)/\partial \rho)$, $(\partial C'(r)/\partial \rho)$ etc. Thus, one may write :

$$\int_{\mathbf{v}} \left[\frac{C'(r)}{\beta} + g_0(r) U'(r) \right] r d\vec{r} = 0 \quad \dots(6)$$

If eqn. (6) is valid for all volumes, the quantity inside the square bracket must vanish, so that

$$C'(r) = -\beta g_0(r) U'(r) \quad \dots(7)$$

Thus, one can write, for the pair potential :

$$U(r) = \frac{1}{\beta} \int_r^\infty \frac{C'(r')}{g_0(r')} dr', \quad \dots(8)$$

where the fact $U(\infty) = 0$ has been utilised. Using the relations (March, 1968) :

$$g(r) - 1 = \frac{1}{2\pi^2 \rho r} \int_0^\infty [S(k) - 1] k \sin kr dk \quad \dots(9)$$

$$C(r) = \frac{1}{2\pi^2 \rho r} \int \left[\frac{S(k) - 1}{S(k)} \right] \cdot k \sin kr dk \quad \dots(10)$$

One can write eqn. (8) as

$$\beta U(r) = \frac{1}{2\pi^2 \rho} \int_r^\infty \left[\frac{1}{r'^2} \int_0^\infty k \left\{ \frac{S(k) - 1}{S(k)} \right\} \times \{kr' \times \right. \\ \left. \cos kr' - \sin kr'\} dk \right] \left/ \left[1 + \frac{1}{2\pi^2 \rho r'} \times \right. \right.$$

$$\int_0^{\infty} \{S(k) - 1\} k \sin kr' dk \Big] dr' \quad \dots(11)$$

Eqn. (11) enables one to calculate $U(r)$ from computed or experimental $S(k)$ data.

RESULTS AND DISCUSSIONS

Effective pair-potential of liquid Neon at 35.05 °K and density 0.03338 atom Å⁻³, calculated by using eqn. (11) and the experimental $S(k)$ data of de Graaf and Mozer (1971) is shown in Fig. 1 along with those calculated by de Graaf and Mozer (1971) using HNC & PY approximations and also Lennard Jones (6, 12) potential with $\epsilon/K_B = 35.5$ K and $\sigma = 2.75$ Å. It can easily be seen from the figure that the present calculation gives a pair potential curve closely similar to that calculated by de Graaf and Mozer (1971) using Lennard-Jones (6, 12) potential while those curves calculated by the same authors using HNC and PY approxi-

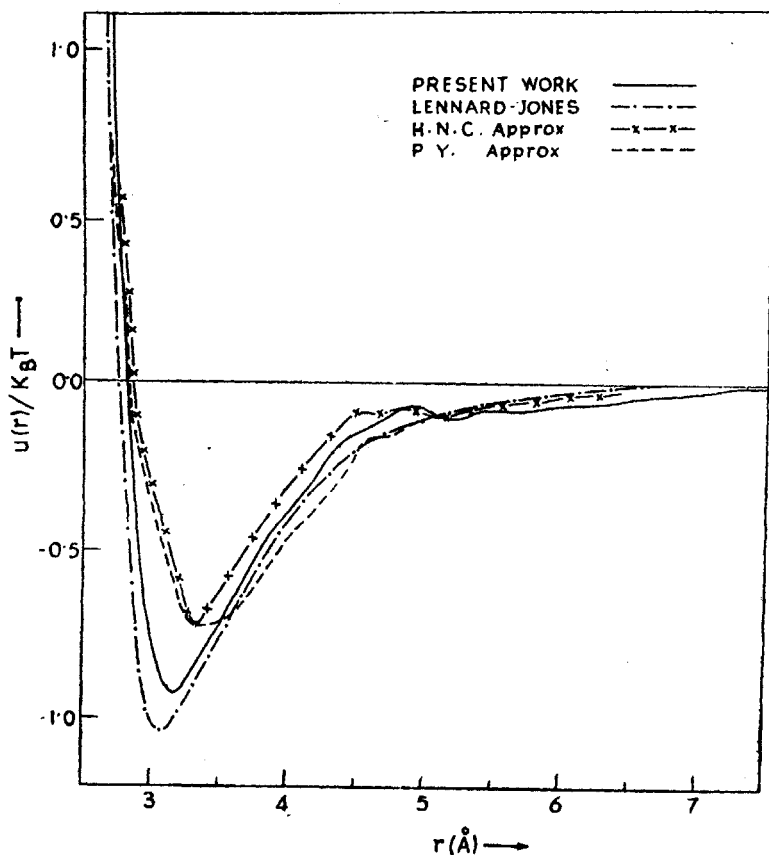


FIG. 1. Effective pair potential of liquid Neon.

mat ions differ very much in every respect from the present curve and Lennard-Jones (6, 12) curve. PY and HNC approximations give erroneous results for dense fluids (de Graaf & Mozer, 1971). Lennard-Jones (6, 12) potential has been accepted as the closest potential function representing pair-potential in a liquid. By proper choice of parameters, ϵ/K_B and σ , it may be possible to bring the calculated LJ curve closer to the presently calculated values. Beyond 4\AA , the present calculation give some minor fluctuations from smoothness. This may be attributed to statistical error in experimental $S(k)$ values as also due to unreliability of $S(k)$ values below $K = 0.4\text{\AA}^{-1}$ which have been calculated through extrapolation using Ping's formula (de Graaf & Mozer, 1971). Some error may also arise due to termination of $S(k)$ values before $K = 0.4\text{\AA}^{-1}$. In the present calculation, the integral has been truncated at $K = 12.8\text{\AA}^{-1}$. But with all these limitations in mind, one can clearly claim that the present method is a very convenient and reliable method of calculating pair-potential.

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