

Extraction of pair-interactions from neutron inelastic scattering data

Ravinder Bansal

*Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 3, 1000 Berlin 33, West Germany
and Iwan N. Stranski Institut, Technische Universität Berlin, Ernst-Reuter-Platz-7, 1000 Berlin 10, West Germany*

P. K. Banerjee* and Narinder K. Ailawadi

Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 3, 1000 Berlin 33, West Germany

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A self-consistent scheme is discussed for calculating the pair potential of simple classical liquids from a knowledge of the zeroth and fourth frequency-moment sum rules of the coherent scattering function $S(q, \omega)$. The procedure is tested by using molecular-dynamics data on a liquid-argon-like system interacting through a Lennard-Jones (6-12) potential. A detailed investigation of the propagation of error in the potential due to uncertainties in the measurement of the data has been made which should serve as a guideline to the experimentalist.

There have been several theoretical attempts to extract some information about the effective pair potential $\phi(r)$ for monatomic liquids from a knowledge of the static structure data measured in diffraction experiments. Among these attempts there are the three well-known approaches correlating the static structure data and the pair potential—the hypernetted chain (HNC), the Percus-Yevick (PY) and the Born-Green (BG) equations. It is found that the potentials obtained from these equations have practically no resemblance with the expected ones.¹ For simple liquids, close to their triple point, both PY and HNC theories yield a potential well which is too shallow by about 40% and whose position is in error by about 10%. The Born-Green equation is even more controversial in that the potentials obtained are not even unique; when q -space inversion technique is used,² the potential is highly temperature dependent in contrast with the almost temperature-independent result obtained in the r space by iteration.³

More recently, Ailawadi and Naghizadeh⁴ proposed a new method to calculate the pair potential $\phi(r)$ for simple liquids from a knowledge of $g(r)$. This technique uses the Singwi *et al.*⁵ theory for the density response function of an interacting electron gas. These authors obtained better results as compared to the three approximate equations discussed above. There are three more schemes available for calculating $\phi(r)$ from the known thermodynamic data and the structure factor. These are the computer simulation method,⁶ the fully thermodynamically consistent integral equation⁷ and perturbation approach.^{8, 9}

The present work is based on the method proposed by Rahman¹⁰ who suggested that a true potential can be obtained provided the zeroth- and fourth-frequency moments of the dynamical structure factor $S(q, \omega)$ are made available by the neu-

tron inelastic scattering experiments for the entire range of momentum transfers. In this paper, we discuss this procedure in more detail and study it for liquid argon. We also discuss the limitations of the method and their possible improvements.

We start with the well-known relation for the fourth moment of $S(q, \omega)$,

$$\langle \omega^4 \rangle = 3\omega_0^4 + \omega_0^2 [\Omega^2(0) - \Omega^2(q)] \quad (1)$$

where

$$\omega_0^2 = q^2 k_B T / m$$

and

$$\Omega^2(q) = \frac{n}{m} \int d\vec{r} g(r) \cos(qx) \frac{\partial^2 \phi(r)}{\partial x^2}. \quad (2)$$

The symbols n , k_B , T , and m have their usual meaning. We introduce another quantity

$$P(q) = -\Omega^2(q) = \langle \omega^4 \rangle \omega_0^{-2} - 3\omega_0^2 - \Omega^2(0), \quad (3)$$

which after carrying out angular integrations reduces to

$$P(q) = -\frac{4\pi n}{m} \int_0^\infty dr r^2 g(r) \phi''(r) j_0(qr) - Q(q), \quad (4)$$

with

$$Q(q) = -\frac{8\pi n}{q^2 m} \int_0^\infty dr g(r) [j_0(qr) - \cos(qr)] \times \left(\phi''(r) - \frac{\phi'(r)}{r} \right). \quad (5)$$

It is found that $P(q)$ is a damped oscillatory function of q (see Fig. 1) and therefore, can be obtained if the neutron scattering results for $\langle \omega^4 \rangle$ are available up to its limiting value. An important point, which is the basis of this calculation, is the fact that a dominant contribution to $P(q)$ comes from the first term on the right-hand side of Eq. (4). This fact allows for an iterative solution of

this equation. As a zeroth-order approximation $Q(q)$ can be neglected, then the inverse Fourier transform of Eq. (4) yields

$$\phi''(r) = -\frac{m}{ng(r)(2\pi)^3} \int d\vec{q} P(q) j_0(qr). \quad (6)$$

$\phi''(r)$ is further integrated between r and ∞ to calculate $\phi'(r)$. The calculated numbers for $\phi''(r)$ and $\phi'(r)$ are in turn used for calculating $Q(q)$ which is added to $P(q)$ to be used for the first-order approximation. The procedure is repeated until self-consistency is achieved. Computational details have been discussed by Rahman¹⁰ in his application of this scheme to liquid rubidium.

We verify the applicability of this method for liquid argon by giving known inputs. First, we calculate $P(q)$ from Eq. (4) by using molecular dynamics data of Verlet¹¹ for $g(r)$ corresponding to a temperature 86.1°K and density $n = 0.02153 \times 10^{24}$ atoms/cm³. It is shown in Fig. 1. Using these numbers for $P(q)$ and iterative scheme described above, we calculate $\phi''(r)$ and $\phi'(r)$. We found that the results for $\phi'(r)$ obtained after seventh iteration were consistent up to four significant figures with those of sixth iteration. The results of $\phi'(r)$ obtained from seventh iteration are then integrated between r and ∞ in order to calculate $\phi(r)$. The resultant potential is shown in Fig. 2 as full curve and is compared with the Lennard-Jones (L-J) potential shown by squares. The marvelous agreement obtained confirms the validity and usefulness of the scheme used.

The main drawback of the scheme is that it requires the data for $\langle \omega^4 \rangle$ for the entire q range (up to $q = 6 \text{ \AA}^{-1}$ for liquid rubidium¹⁰ and $q = 10 \text{ \AA}^{-1}$ for liquid argon). We investigate the effect of truncating $P(q)$ [i.e., setting $P(q) = 0$] at $q = 6, 8,$ and 10 \AA^{-1} . The resultant potentials $\phi(r)/\epsilon$ are found to have well depths 1.26, 0.93, and 0.98,

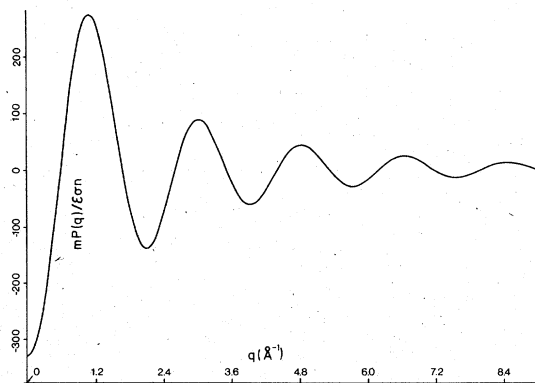


FIG. 1. $mP(q)/\epsilon n$ vs q with $n = 0.02153 \times 10^{24}$ atoms/cm³, $\epsilon = 119.8^\circ\text{K}$, $\sigma = 3.405 \text{ \AA}$.

respectively. The effect of cutoff after $q = 10 \text{ \AA}^{-1}$ is found insignificant in the potentials.

It is well-known that accurate experimental measurement of $\langle \omega^4 \rangle$ becomes extremely difficult, in particular for very-small-momentum and large-energy transfers. The only attempt to measure $\langle \omega^4 \rangle$ from neutron scattering data is by Suck.¹² But his estimates for $\langle \omega^4 \rangle$ for liquid Rb are poor because of the large errors in the wings of $S(q, \omega)$. Furthermore, the smallest q investigated by him is 1.0 \AA^{-1} . However, Copley and Rowe¹³ have been able to perform measurements for q as small as 0.3 \AA^{-1} , but the measured $S(q, \omega)$ is not very reliable at small q and ω .

In the presence of such difficulties, one would like to have some alternative method for estimating $\langle \omega^4 \rangle$. It is found that the dominant contribution to the fourth-moment integral arises from the term $r^2 g(r) \phi''(r)$. Physically, this quantity describes the spatial range of correlation of forces which is very small and is peaked near the hard-core radius R_0 . Hubbard and Beeby¹⁴ have proposed that a good approximation to $\langle \omega^4 \rangle$ can be obtained by replacing the product $r^2 g(r) \phi''(r)$ by a δ function at $r = R_0$ with the weight

$$\omega_E^2 = \frac{n}{m} \int d\vec{r} g(r) \frac{\partial^2 \phi(r)}{\partial x^2} = \Omega^2(0), \quad (7)$$

and neglecting the term proportional to $\phi'(r)$. This gives

$$P(q) = -3\omega_E^2 (qR_0)^{-3} [(qR_0)^2 \sin(qR_0) + 2(qR_0) \cos(qR_0) - 2 \sin(qR_0)]. \quad (8)$$

The only unknown in Eq. (8) is the frequency ω_E , which can be recognized as the maximum phonon frequency in a solid close to its melting point. We already demand above, Eq. (6), that in order to determine $P(q)$, $\langle \omega^4 \rangle$ should be measured up to its limiting value, then $\langle \omega^4 \rangle = 3(q^2 k_B T / m) + \omega_E^2$. Furthermore, using the δ -function approximation, Suck¹² fitted his results $\langle \omega^4 \rangle$ for liquid rubidium and obtained $R_0 = 4.8 \text{ \AA}$ and $\omega_E = 0.65 \times 10^{13} \text{ sec}^{-1}$. On the other hand, if one estimates ω_E from the Debye temperature ($\Theta_D = 56^\circ\text{K}$) for crystalline rubidium, it comes out to be $0.73 \times 10^{13} \text{ sec}^{-1}$ which is very close to the value obtained by Suck (see also Ref. 15).

Even though the approximate Eq. (8) in itself is not capable of yielding information about $\phi(r)$, $P(q)$ obtained from this equation together with neutron diffraction data for $g(r)$ may, in principle, be used in Eqs. (4)–(6) to extract the potential. We used $R_0 = 3.405 \text{ \AA}$ and $\omega_E = 0.77 \times 10^{13} \text{ sec}^{-1}$ obtained by Levesque *et al.*¹⁶ through the molecular-dynamics simulation of a Lennard-Jones system. We found that Eq. (8) is a very good representation

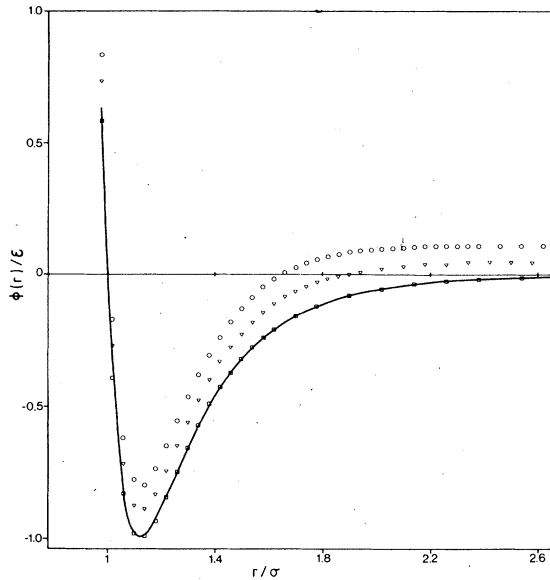


FIG. 2. $\phi(r)/\epsilon$ vs r/σ . Squares: L-J potential, full curve: potential obtained with present scheme, triangles: potential obtained with 1% random error in $P(q)$, circles: potential obtained with 2% random error in $P(q)$.

of $P(q)$ for q up to about 0.5 \AA^{-1} after which it starts deviating slowly from its exact value. These deviations increase with increasing q thereby leading to a failure of the iterative procedure and the resulting potential comes out to be very absurd. This is because the large- q value of $P(q)$ strongly reflects in the small- r behavior of $\phi''(r)$ which in turn spoils $Q(q)$. It is, therefore, recommended that Eq. (8) for $P(q)$ should not be used as input for all q values. However, one can safely use Eq. (8) for smaller momentum transfers (q up to about 0.5 \AA^{-1} in liquid argon) which cannot be probed with a sufficient accuracy by neutron scattering experiments. Therefore, if the neutron scattering experiments are capable of providing an accurate information about $\langle \omega^4 \rangle$ for $q \leq 0.5 \text{ \AA}^{-1}$, the iterative procedure given by Eqs. (4)–(6) should be successful in determining $\phi(r)$.

An immediate question which an experimentalist would like to be answered is how accurate should be the data for $\langle \omega^4 \rangle$ and $g(r)$ in order to get a reasonably accurate potential through the present scheme? In what follows, our main task would be to answer this question.

In order to decide the accuracy of the $\langle \omega^4 \rangle$ or $P(q)$ data, we first introduce errors in $P(q)$ (shown in Fig. 1). We use a random function generator which yields random numbers between -0.5 and 0.5 . We introduce an error of 1%, i.e., a particular $P(q)$ value can lie anywhere between

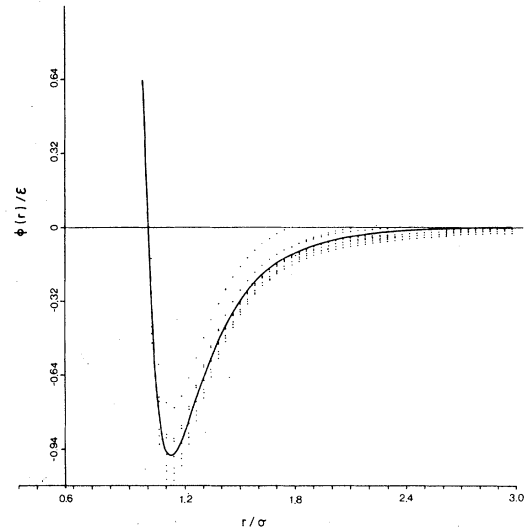


FIG. 3. $\phi(r)/\epsilon$ vs r/σ for various data sets for $P(q)$ which are all randomly erroneous by 1%. Solid curve is the result with original data for $P(q)$.

$0.995P(q)$ and $1.005P(q)$ depending on the random number. Using this new set of $P(q)$ values and original data for $g(r)$, we again iterate Eq. (4) to solve for $\phi(r)$. The resultant potential is shown in Fig. 2 by triangles. We then increase the error to 2% and repeat the calculation for $\phi(r)$ which is also shown in Fig. 2 by open circles. In the second case (2% error), the random numbers used were same as for the first case (1% error). Resultant potential with 2% error in $P(q)$ is systematically deviated from the first one [with 1% error in $P(q)$]. We can only conclude that the scheme is sensitive to even small errors in $P(q)$ data.

In Fig. 3, we plot the results of $\phi(r)$ obtained using various data sets for $P(q)$ which are all randomly erroneous by 1%. The random numbers used in each data set are different from each other. We calculate $\phi(r)$ using *nine* different data sets for $P(q)$ including the original data. As stated above we do not change $g(r)$ data. The full curve in Fig. 3 represents the result with original data for $P(q)$ and the points are with eight other data sets. The purpose of this figure is to show that if an experimentalist is able to provide the data for $P(q)$ by repeating his experiment several times for each q , then the scheme can be used to extract a reliable potential.

We also investigate the effect of propagation of error in $\phi(r)$ due to uncertainties in $g(r)$. As in the case of $P(q)$, we deliberately introduce random errors in $g(r)$ while keeping $P(q)$ unchanged. In Fig. 4 we have displayed these results. The solid lines in the two diagrams represent $g(r)$ and $\phi(r)/\epsilon$ with no error in $g(r)$ or $P(q)$. The triangles and open

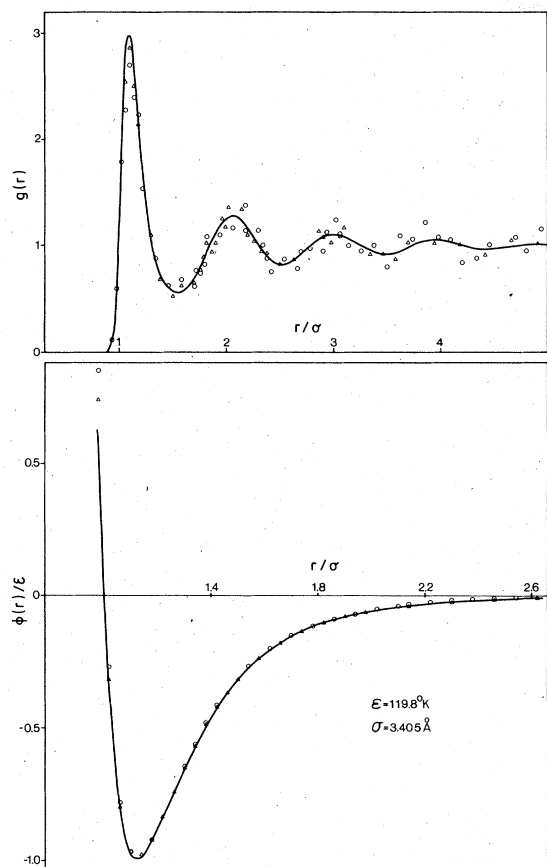


FIG. 4. $g(r)$ vs r/σ and $\phi(r)/\epsilon$ vs r/σ . Solid curve: $g(r)$ and $\phi(r)/\epsilon$ with no error in $g(r)$, triangles and circles are results corresponding to 10% and 20% error introduced randomly in $g(r)$.

circles are the results of 10% and 20% error introduced in $g(r)$ randomly while $P(q)$ was left unchanged. As can be seen from this diagram there is no significant difference in the resulting potentials.

These results are not controversial because in our scheme we use the values of $g(r)$ from molecular dynamics data in Eq. (4) to obtain $P(q)$ and once $P(q)$ is computed we keep that unchanged in

the successive iterations to calculate the potential. Thus when errors are introduced in $g(r)$, this changed $g(r)$ used in Eq. (6) affects $\phi''(r)$ and consequently $\phi'(r)$ which are further used in Eq. (5) to calculate $Q(q)$. Note that this effect of $g(r)$ in $\phi''(r)$ exactly cancels out in $Q(q)$. Since $\phi'(r)$ contains an integrated effect of $g(r)$, it does not cancel out in $Q(q)$. But this latter effect is known to be very small as compared to that of $\phi''(r)$. Thus it is not surprising that even large errors in $g(r)$ (in this calculation) do not affect the potential significantly.

We conclude from the present as well as Rahman's analysis that the self-consistent scheme described here can be directly applied to extract reliable pair potentials from neutron scattering data for both the rare-gas liquids and liquid metals containing coherent and incoherent contributions.

Since the method described here is solely dependent on the availability of accurate data for $\langle \omega^4 \rangle$ and $g(r)$, our analysis shows that in order to extract a correct potential it may be necessary to have several data sets with known accuracy (Fig. 3). If however only one set of data is available, $\langle \omega^4 \rangle$ should be as accurate as 1% if at all a reliable potential is to be extracted from the present scheme. We find that the approximate expression (8) is a good representation of actual $P(q)$ for q up to 0.5 \AA^{-1} —a comparatively inaccessible region to be probed by the neutron scattering experiments. Therefore, efforts should only be directed towards obtaining accurate data for $\langle \omega^4 \rangle$ for q between 0.5 and 10 \AA^{-1} .

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*Permanent address: Physics Dept., R. I. Jr. College, Warwick, R. I. 02887.

¹See, for example, R. O. Watts, in *Specialist Periodical Report: Statistical Mechanics*, edited by K. Singer (British Chemical Society, London, 1973), Vol. I.

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