Comments and Addenda

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Determination of pair interactions from neutron inelastic scattering data*

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Neutron inelastic scattering data from a monatomic liquid can be directly translated into a pair interaction. This requires accurate experimental determination of the zeroth and fourth moments of $S(\kappa,\omega)$. The iterative calculation works because the Fourier transform of the fourth moment gives a good zeroth approximation to the second derivative of the potential. Recent molecular dynamics data on liquid rubidium are used to illustrate the method. Experiments should be carried out to exploit this method.

The experimental technique of neutron inelastic scattering provides detailed information about fluctuations of density and also about diffusive motion of the particles in the system. In the case of liquid systems, comparison of the experimental results with molecular dynamics calculations, which require an assumed interparticle potential, has been used as an indirect check on the validity of the potential assumed. The first case of this kind was of course liquid argon[1,2]; recently liquid rubidium has also given encouraging results.[3,4]

The purpose here is to show that a neutron experiment is by itself capable of yielding the pair interaction in a monatomic liquid; in case multibody forces are present in the Hamiltonian but are relatively less important, one would obtain an effective two-body approximation for the Hamiltonian. Further discussion is relegated to the end of the note.

Neutron experiments, after careful reduction of the raw data, yield $S(\kappa,\omega)$ the dynamical scattering function; $\hbar\kappa$ and $\hbar\omega$ are, respectively, the momentum and energy change of the scattered neutron. For liquids only the magnitude κ is relevant. After removing the detailed balance factor $\exp(-\hbar\omega/2k_BT)$, the scattering function becomes symmetric in ω, and in many cases of interest the symmetrized function has negligible quantum contribution. For very light nuclei and for very large κ the recoil term $\exp(-\hbar^2\kappa^2/8Mk_BT)$ may have to be considered as well. In the following we shall consider the symmetrized function in purely classical terms.

Let us assume that the experiment is detailed and accurate enough to provide us with the first three even moments of $S(\kappa,\omega)$, to be denoted, respectively, by $\langle\omega^0\rangle$, $\langle\omega^2\rangle$, and $\langle\omega^4\rangle$. Now $\langle\omega^0\rangle \equiv S(\kappa)$ is the structure factor, its Fourier transform being the pair correlation $g(r)$. $\langle\omega^2\rangle$ is just κ^2k_BT/M, T being the temperature, M the mass of the particles. $\langle\omega^4\rangle$ can be written in terms of the number density ρ, $g(r)$, and the pair potential $\psi(r)$, assuming only pair interactions in the Hamiltonian (de Gennes[5]). Let $\omega_l^2 = \langle\omega^4\rangle/\langle\omega^2\rangle$. The notation used here is given in Ref. 6. We have

$$\omega_l^2 = 3\kappa^2k_BT/M + \Omega^2(0) - \Omega^2(\kappa), \tag{1}$$

$$\Omega^2(\kappa) = (\rho/M)\int d\vec{r}\, g(r)\cos\kappa x\, \partial^2\psi/\partial x^2 . \tag{2}$$

For large κ, $\Omega^2(\kappa) \to 0$. We assume that ω_l^2 has been measured to its limiting value, namely $3\kappa^2k_BT/M + \Omega^2(0)$, so that $P(\kappa) = \omega_l^2 - 3\kappa^2k_BT/M - \Omega^2(0)$ is available over the whole range of κ, and, of course, vanishes at large κ. We get

$$P(\kappa) = -\frac{\rho}{M}\int d\vec{r}\, g(r) j_0(\kappa r)\psi''(r) + \frac{2\rho}{M}\int d\vec{r}\, g(r)\left[j_0(\kappa r) - \cos\kappa r\right]\frac{(\psi'' - \psi'/r)}{\kappa^2r^2}. \tag{3}$$

Here $j_0(\kappa r)$ is $(\sin\kappa r)/\kappa r$; ψ' and ψ'' are the derivatives of $\psi(r)$.

The central point of this note is that the first

TABLE I. $[\psi(r)]_n$ and $[\psi''(r)]_n$ where n is the iteration number, r the distance in units of 4.4048 Å. Rows marked ψ or ψ'' give the true potential and its second derivative. The unit of energy is 555.89×10^{-16} ergs. Below $r=0.8$, ψ'' can probably be improved by using a better algorithm in the numerical integration.

$n\backslash r$	0.76	0.80	0.90	1.0	1.2	1.4	1.6	1.8	2.0	2.2
0			291	99	30	−1.5	−6.6	−3.4	−0.05	0.89
1			103	137	31.6	−4.36	−8.36	−3.51	0.151	0.985
8	5207	73	255	142	30.8	−5.18	−8.42	−3.45	0.174	0.971
ψ''	469	400	247	141	30.7	−4.96	−8.37	−3.42	0.169	0.972
ψ	9.93	7.27	2.31	−0.0453	−0.981	−0.468	−0.0409	0.0641	0.0290	−0.008 94
8	9.35	6.99	2.22	−0.0562	−0.984	−0.460	−0.0435	0.0623	0.0268	−0.0105

$n\backslash r$	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2
0	0.43	−0.11	−0.24	−0.068	0.084	0.091	0.013	−0.045	−0.027	−0.003
1	0.397	−0.163	−0.256	−0.0585	0.0954	0.0863	0.006 20	−0.0508	−0.0271	0.0034
8	0.382	−0.168	−0.253	−0.0572	0.0914	0.0862	0.003 37	−0.0500	−0.0275	0.0034
ψ''	0.381	−0.170	−0.251	−0.0551	0.0927	0.0877	0.002 14	−0.0486	−0.0339	0.0070
ψ	−0.0129	−0.001 08	0.005 78	0.003 56	−0.001 06	−0.002 65	−0.000 97			
8	−0.0137	−0.001 44	0.005 47	0.003 28	−0.001 34	−0.002 81	−0.001 10			

term on the right-hand side of Eq. (3) gives the main contribution to $P(\kappa)$. For the moment accepting this statement as correct, and using the fact that ψ' and ψ'' vanish for large r, we see the possibility of an iterative solution of Eq. (3). We write Eq. (3) as

$$P(\kappa)+Q(\kappa)=-(\rho/M)\int d\vec{r}\, g(r)j_0(\kappa r)\psi''(r). \qquad (4)$$

The zeroth approximation for $\psi''(r)$ is obtained from the Fourier transform of $P(\kappa)$. Introducing this and its integral $\psi'(r)$ into $Q(\kappa)$, we get the next approximation to $\psi''(r)$ from the Fourier transform of $P(\kappa)+Q(\kappa)$, and so on. Of course $\psi''(r)$ cannot be obtained for small values of r, for which $g(r)$ vanishes.

The method has been tested by using the recent molecular-dynamics calculations[4] on liquid rubidium. Unfortunately the neutron experiments[3] were not directed towards a determination of $\langle\omega^4\rangle$. Hence $P(\kappa)$ and $g(r)$ given by molecular dynamics have been used as input for justifying the assertions made above. A plot of $P(\kappa)$ can be inferred from Fig. 3 of Ref. 4.

Table I gives the results. The line marked n gives the nth approximation to $\psi''(r)$, namely $[\psi''(r)]_n$. $n=0$ already shows a fair representation of the true $\psi''(r)$ (line marked ψ''). For insertion into $Q(\kappa)$, $[\psi''(r)]_0$ is put equal to zero below $r=0.93$ (units are shown in caption for Table I); $[\psi'(r)]_0$ is calculated as $-\int_r^\infty[\psi''(r)]_0\,dr$. Then the transform of $P(\kappa)+Q(\kappa)$ is on line 1. The improvement is obvious. As the iterations proceed, $[\psi''(r)]_n$ is put equal to zero at successively lower values of r, namely 0.90, 0.86, 0.84, 0.82, 0.80, 0.78, 0.76. The values of $g(r)$ below 0.76 are zero. Note that the only region which defies gradual improvement is below 0.80. The last two lines show the function $\psi(r)$ and the values obtained for the potential from the final iteration (No. 8). A trapezoidal integration with $r=0.002$ was used throughout.

In conclusion we note the following:

(i) For mixed coherent and incoherent scatterers (e.g., Na, Ar) the basic equation becomes $(\sigma_c+\sigma_i)\sigma_c^{-1}[\omega_l^2-3\kappa^2kT/M-\Omega^2(0)]=-\Omega^2(\kappa)$, and is therefore directly applicable even in this case. ω_l^2 now stands for the ratio of the fourth and the second moment of $\sigma_cS_{\rm coh}+\sigma_iS_{\rm inc}$, where σ_c and σ_i are the coherent and incoherent scattering cross sections, respectively. If $\sigma_c\ll\sigma_i$ (as for protons), the method will fail because ω_l^2 will be almost equal to $3\kappa^2kT/M+\Omega^2(0)$.

(ii) The experimental requirements are twofold. First, an accurate diffraction experiment is needed to get $g(r)$ analogous to Yarnell's experiments[7] with liquid argon. Second, an inelastic scattering experiment is needed which is tuned not to high resolution for the quasielastic region, but to low resolution and high intensity in the inelastic region relevant to the determination of the fourth moment. In liquid rubidium, for example, this implies covering a range of κ up to 6 Å^{-1}, with ω going up to about 50 psec^{-1} ($\hbar\omega\approx30$ meV) around $\kappa=6$ Å^{-1} and much less for smaller κ's. It is hoped that experimental work along these lines will soon be attempted.

(iii) In argon where two- and three-body terms in the Hamiltonian have been successfully worked out,[8] the above treatment should give an effective pair interaction; comparison of this with the much

used L-J potential for argon should be enlightening.

(iv) For systems where quantum effects are not negligible the above formulation still holds when cast in terms of the third moment of a suitably modified unsymmetrized $S(\kappa, \omega)$.[9]

(v) Since $g(r)$ and hence $S(\kappa)$ are known to be sensitive mainly to the repulsive part of the interaction, it appears that $\langle\omega^4\rangle$ is a key experimental quantity for the determination of the potential in the attractive region.

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