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Effective-Field Approximations in Classical Liquids

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Three recent approximate theories of coherent scattering of slow neutrons in classical liquids are compared. Close connections are established among them which allow a considerable simplification in the computations needed to compare them with experiment.

There have been several recent approximate theories for the coherent scattering of slow neutrons by simple classical liquids. Two of these[1,2] start from a modified random-phase approximation (RPA). A third[3] is phrased directly in terms of the space-time correlation functions $G(r,t)$. References 1 and 3 calculate the Laplace transform of the intermediate scattering function

$$F(q,\omega)=\int_0^\infty e^{i\omega t}\langle\rho_q(t)\rho_{-q}(0)\rangle\,dt \tag{1}$$

for ω in the upper half-plane. Reference 2 calculates the density-density response function $\chi(q,\omega)$. Using standard methods[4] of linear response theory, one can relate these two functions by

$$\beta^{-1}\chi(q,\omega)=i\omega F(q,\omega)-S(q), \tag{2}$$

where $S(q)$ is the usual structure factor and $\beta^{-1}=kT$.

When expressed in terms of $\chi(q,\omega)$ all of the results in Refs. 1–3 can be put in the form

$$\chi(q,\omega)=\frac{\chi_{sc}(q,\omega)}{1-\psi(q)\chi_{sc}(q,\omega)}. \tag{3}$$

The approximations in each of these papers can be stated in terms of the results obtained for $\psi(q)$ and $\chi_{sc}(q,\omega)$. The neutron scattering cross section is then determined from

$$S(q,\omega)=-(\pi\beta\omega)^{-1}\chi''(q,\omega) \tag{4}$$

for real ω. The real and imaginary parts of $\chi(q,\omega)$ for real ω are denoted by $\chi'(q,\omega)$ and $\chi''(q,\omega)$, respectively. These are related by the usual Kramers-Kronig relations.[5] In particular,

$$\chi(q,0)=\chi'(q,0)=\pi^{-1}\int_{-\infty}^{+\infty}\omega^{-1}\chi''(q,\omega)d\omega=-\beta S(q). \tag{5}$$

The approximate theories discussed here all have $\chi_{sc}(q,0)=-\beta$ so that Eqs. (3) and (5) imply

$$S(q)=[1+\beta\psi(q)]^{-1}. \tag{6}$$

The simplification afforded by Eq. (6) was overlooked in Ref. 2, but plays an essential role here.

The conventional RPA corresponds to taking the ideal gas value $\chi^g(q,\omega)$ for χ_{sc} and the Fourier transform $v(q)$ of the interatomic potential for $\psi(q)$. In Ref. 1 this was modified by taking $\psi(q)=-\beta^{-1}c(q)$, where $c(q)=[S(q)-1]/S(q)$ is the Fourier transform of the direct correlation function. This just modifies the RPA result so as to give the correct static structure. The result for $S(q,\omega)$ is given in closed form in Eq. (13) of Ref.

1. The theoretical basis for this result is now better understood.[6] In Ref. 2 the first approximation discussed is derived in a dynamically well-defined way,[7] and gives Eq. (3) with χ_{sc} given by χ^g, and $\psi(q)$ given as a prescribed linear functional of the radial distribution function $g(r)$. [See Eq. (6) of Ref. 2.] Equation (6) of Ref. 2 combined with Eq. (6) above allow $S(q)$ to be calculated self-consistently, as emphasized in Ref. 7. The computation presented in Ref. 2 is, however, only the first iteration in such a procedure starting from a molecular dynamics calculation for $g(r)$. The numerical result after this first iteration does not appear to be of any physical interest. This approximation differs from Ref. 1 only in that Ref. 1 uses the experimental structure factor for $S(q)$ whereas Ref. 2 if consistently carried out would use a theoretical structure factor calculated as discussed above.

The result of Kerr[3] when expressed in terms of $\chi(q,\omega)$ corresponds to taking $\psi(q) = -\beta^{-1}c(q)$ as in Ref. 1, but gives for χ_{sc} the value $\chi^S(q,\omega)$ associated with the exact motion of a single particle. A second approximation presented in Ref. 2 is closely related to this. $\chi_{sc}(q,\omega)$ is approximated by $\chi^S(q,\omega)$ without justification, and $\psi(q)$ is given by [Eq. (7) of Ref. 2] a linear functional of the radial distribution function. When combined with Eq. (6) of this paper, this again defines a theoretical $S(q)$ to be calculated self-consistently. This has not yet been done. The result that would finally be obtained for $\chi(q,\omega)$ is, however, the same as in Ref. 3 with the exception that the theoretically determined $S(q)$ would be used in place of the experimental value.

Thus the results presented in Ref. 2 are essentially equivalent to those obtained in Refs. 1 and 3. Reference 2 has the theoretical advantage that it defines an approximate calculation of the structure as well as of the dynamics. This advantage has not yet, however, been exploited.

In actual computation one needs the real and imaginary parts of $\chi^S(q,\omega)$. These are obtained from the sine and cosine transforms of the intermediate scattering function $F_S(q,t)$. The final expression for $S(q,\omega)$ is

$$S(q,\omega) = S_S(q,\omega) \times \{[1 - c(q) + \pi\omega c(q) R_S(q,\omega)]^2 + [\pi\omega c(q) S_S(q,\omega)]^2\}^{-1}, \tag{7}$$

where

$$S_S(q,\omega) = \frac{1}{\pi}\int_0^\infty \cos\omega t F_S(q,t)dt,$$

$$R_S(q,\omega) = \frac{1}{\pi}\int_0^\infty \sin\omega t F_S(q,t)dt,$$

and $$F_S(q,t) = \langle e^{-i\vec{q}\cdot\vec{r}_1(t)} e^{i\vec{q}\cdot\vec{r}_1(0)}\rangle .$$

Equation (7), though not given explicitly in Ref. 3, follows trivially from Kerr's final result. That it is also the result of Ref. 2 is less obvious, and is in fact the main point of this paper. Actual computations with Eq. (7) are not difficult if one is working with the results of molecular dynamics computations. Such computations are now in progress at this laboratory.[8] The physics of Eq. (7) is that of a modified convolution approximation relating the motion of one particle to the motion of a density disturbance. This is most easily seen by breaking $\chi(q,\omega)$ into self and distinct parts, $\chi_S(q,\omega)$ and $\chi_d(q,\omega)$. This can be done by introducing an external potential which couples only to the density of the test particles. The density response of the test particle is given by $\chi_S(q,\omega)$ and that of the other particles by $\chi_d(q,\omega)$. Kerr's approximation can be concisely expressed in the form

$$\chi_d(q,\omega) = -\beta^{-1}c(q)\chi(q,\omega)\chi_S(q,\omega). \tag{8}$$

If in Eq. (8) $\chi(q,\omega)$ is replaced by $\chi(q,0)$, one recovers the original convolution approximation proposed by Vineyard.[9] It is suggestive from Eq. (8) that Kerr's approximation can be more simply stated physically than in Ref. 3, but no progress in this direction can yet be reported.

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