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ZERO SOUND IN CLASSICAL LIQUIDS[*]

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Starting from a zero-sound approach, a calculation of the spectral function of the current-current correlation, which is valid at short wavelengths and high frequencies, is given for classical liquids. The theory is used to explain results of neutron inelastic scattering in liquid argon.

Recently, Pines[1] has advanced arguments for the existence of a zero-sound mode in liquid He^3 and He^4 over a wide temperature range—a range in which neither Landau's theory of Fermi liquids is applicable (for He^3) nor He^4 is a superfluid. These considerations led Pines to conjecture that a zero-sound mode at short wavelengths and high excitation frequencies might be a quite general liquid property. This suggestion of Pines has hitherto not been investigated in any quantitative manner for the case of classical liquids. Rather, experimentalists have used phenomenological models[2,3] to explain neutron inelastic scattering results.

The purpose of this Letter is twofold: (i) to present experimental data for the spectral function of the current-current correlation function in liquid argon, and (ii) to develop a theory based on Pines' suggestion and compare its consequences with experiment. The theory is reasonably successful and opens up the possibility for further applications.

In contrast to the hydrodynamic case, the restoring force responsible for the zero-sound mode is the average self-consistent field of all the particles acting in concert, as for plasmons in an electron liquid. The average polarization potential corresponding to this restoring force is defined by

$$\varphi_{\mathrm{pol}}(\vec{q},\omega)=\psi(\vec{q})\langle\rho(\vec{q},\omega)\rangle, \qquad (1)$$

where $\psi(\vec{q})$ is to be determined later and $\langle\rho(\vec{q},\omega)\rangle$ is the Fourier transform of the average fluctuation in the particle density. The density-density response function is given by[1]

$$\chi(\vec{q},\omega)=\frac{\chi_{sc}(\vec{q},\omega)}{1-\psi(\vec{q})\chi_{sc}(\vec{q},\omega)}. \qquad (2)$$

Here $\chi_{sc}(\vec{q},\omega)$ is a measure of the response to both the external and the polarization field. The problem is to determine $\chi_{sc}(\vec{q},\omega)$ and $\psi(\vec{q})$.

We make the physical assumption that $\chi_{sc}(\vec{q},\omega)$ is determined by the single-particle motion. As is well known , this motion resembles that of a gas of free particles for large q values, whereas for smaller q values it is both diffusive and vibratory in nature. The imaginary part of χ_{sc} is then related to the dynamic form factor $S_s(\vec{q}, \omega)$ for the self-motion through the equation

$$\operatorname{Im}\chi_{sc}(\vec{q},\omega) \simeq -\pi n(\omega/k_B T) S_s(\vec{q},\omega), \tag{3}$$

since $\hbar\omega \ll k_B T$ for the frequencies of interest. The quantity n is the number density. For a free gas, neglecting recoil, one has $S_s{}^g(\vec{q}, \omega) = (M/q^2 2\pi k_B T)^{\frac{1}{2}} \exp(-M\omega^2/2q^2 k_B T)$. Substituting this in (3) and making use of the Kramers-Kronig relation, one obtains

$$\operatorname{Re}\chi_{sc}{}^g(\vec{q},\omega) = -(n/k_B T)\{1 + i(M\pi\omega^2/2q^2 k_B T)^{\frac{1}{2}} \exp(-M\omega^2/2q^2 k_B T) \operatorname{erf}[i(M\omega^2/2q^2 k_B T)^{\frac{1}{2}}]\}. \tag{4}$$

On the other hand, for finite frequencies and small q values one has[4] $S_s(\vec{q},\omega) \simeq (k_B T q^2/2M\omega^2) f(\omega) + O(q^4)$, where $f(\omega)$ is the Fourier transform of the normalized velocity autocorrelation function. Using the analytic representation[5] of $f(\omega)$ as computed by Rahman,[6] one similarly obtains, in the small-q limit,

$$\operatorname{Re}\chi_{sc}{}^d(\vec{q},\omega) = (nq^2 D/\pi k_B T)[(-i\pi/\omega)\exp(-\omega^2/\omega_0{}^2)\operatorname{erf}(i\omega/\omega_0) - A'\omega_m$$
$$+ 2A'\omega \int_0^\infty dy \sin(2\omega y/\omega_m)(1+y^2)^{-1}], \tag{5}$$

where the parameters[5] occurring in $f(\omega)$ are $\omega_0 = 0.25 k_B T/\hbar$, $\omega_m = 0.37 k_B T/\hbar$, and $A' = 61.48(\hbar/k_B T)^2$, and $\boldsymbol{D}$ is the diffusion coefficient. It might be mentioned that the above separation of $\chi_{sc}(\vec{q},\omega)$ for large and small q values is, in principle, not necessary if one has a complete knowledge of $S_s(\vec{q},\omega)$, i.e., of self-motion.

Our next problem is to determine $\psi(\vec{q})$ of Eq. (1). For this purpose we approximate the non-random-phase-approximation terms in the equation of motion[7] for the density fluctuation $\rho_{\vec{q}}$ in the manner suggested by Singwi et al.[8] for the case of an electron liquid. This procedure takes approximately into account local field corrections which in the present case, where we are dealing with a hard-core potential, are of primary importance. The expression for $\psi(\vec{q})$ obtained in Ref. 8 can be written in the form

$$\psi(\vec{q}) = -\frac{4\pi}{q^3}\int_0^\infty [\sin(qr) - qr\cos(qr)] g(r) \frac{d\varphi(r)}{dr} dr. \tag{6}$$

In the present case $\varphi(r)$ is the 6:12 Lennard-Jones potential and $g(r)$ is the equilibrium pair-distribution function. Equation (6) has been found[8] to be a reasonable approximation for large values of q. For small values of q, on the other hand, a better approximation for $\psi(\vec{q})$ is

$$\psi(\vec{q}) = -\frac{4}{3q^3}\int_0^\infty [\sin(qr) - qr\cos(qr)] g(r) \left[\frac{d\varphi(r)}{dr} - \frac{1}{2} r \frac{d^2\varphi(r)}{dr^2}\right] dr, \tag{7}$$

which, from the equation of motion[7] for $\rho_{\vec{q}}$, can be shown to be exact in the limit $q \to 0$. We are unable to estimate the correction to Eq. (6) which will bring it into agreement with Eq. (7) in the limit of small q. However, it was found that this correction is of importance only in a narrow region of q, around $q = 1.8$ Å^{-1}, where $\psi(\vec{q})$ of Eq. (6) is large and negative. We have, therefore, added a constant term to Eq. (6); the value of the constant $(0.6 k_B T/n)$ was obtained by requiring that the theory should reproduce the height of the first peak of the structure factor $S(q)$ as obtained by Rahman.[9]

Having thus obtained expressions for χ_{sc} and $\psi(\vec{q})$, we can calculate $\operatorname{Im}\chi(\vec{q},\omega)$ from Eq. (2) and hence $S(\vec{q},\omega)$. We have evaluated numerically the function $\omega^2 S(\vec{q},\omega)$, which is the spectral function of the longitudinal current-current correlation, as a function of ω for a set of q values ranging from 0.2 to 4 Å^{-1}. In the computations, the values of $g(r)$ obtained by Rahman[9] were used. For each value of q the spectral function has a maximum. In Fig. 1(b) we have plotted the frequency (denoted by $\omega_{\max}$) corresponding to this maximum as a function of q. In the same figure the crosses denote the experimental values[10] of Sköld, and the solid circles are the computer re-

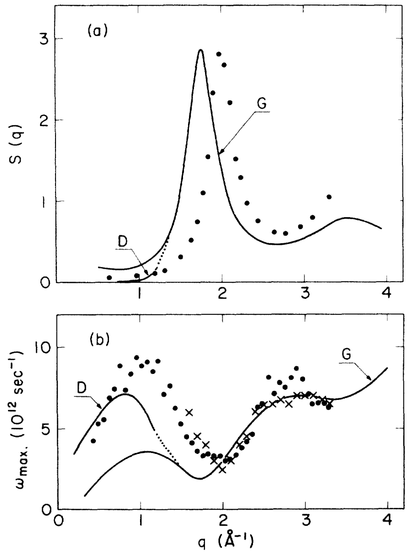

FIG. 1. (a) $S(q)$ vs q, and (b) $\omega_{\max}$ vs q in liquid argon. The crosses are the results based on the experimental data of Sköld and Larsson (Ref. 10) and the solid circles are those of Rahman (Ref. 11) based on machine computations. The theoretical curves marked G are the results of the present calculations using the gas model for χ_{sc} [Eq. (4)] and $\psi(\underset{\sim}{q})$ of Eq. (6) with the constant correction discussed in the text, assumed valid for all q values. The curves marked D are the results of the present calculations using the expression valid in the small-q limit for χ_{sc} [Eq. (5)] and $\psi(\underset{\sim}{q})$ of Eq. (7). The two regions have been smoothly joined by the dotted curve. The present results and the results of Rahman are for 76°K, while the results of Sköld and Larsson are for 94°K.

sults of Rahman.[11] In Fig. 1(a) the solid curve gives the calculated structure factor and solid circles are the results of Rahman.[11] The calculated spectral function as a function of ω for different q values also agrees reasonably well with Rahman's computations.[11] The second moment relation is exactly satisfied by our $S(\vec{q},\omega)$. In view of the fact that, except for the comparatively minor correction to Eq. (6), there are no adjustable parameters in the theory, the agreement with the experimental results must be considered rather good. It may be noted that the minimum in $\omega_{\max}(q)$ and the maximum in $S(q)$ occur at the same value of q, which is also the case in the experimental data. The shift of the theoretical curves relative to the experimental curves probably arises from our lack of knowledge of the precise q dependence of the correction term in $\psi(\vec{q})$ of Eq. (6).

Recently there has been considerable interest[11,12] in the plot of $\omega_{\max}$ vs q arising out of a suggestion by Zwanzig[13] (inspired from hydrodynamic analogy) that the Fourier component of the current should have the characteristics of a collective coordinate. It must, however, be borne in mind that only in the limit $q \to 0$ can such a plot be unambiguously identified as the dispersion curve for the collective modes.

The plateau of the curve of Fig. 1(b) in the region 2.5 $\text{Å}^{-1} \leq q \leq 3.4\ \text{Å}^{-1}$ has a striking resemblance[14] to that in the dispersion curve in liquid He II. In the present formulation this plateau is the result of the local field correction typical of a hard-core potential, and therefore its occurrence should be a very general property for liquids with an interatomic potential which has a hard core. It would be of considerable interest to test the present theory against experimental data[15] on inelastic neutron scattering in He I. The success of the present approach also prompts us to calculate the pair correlation function in liquid He^3 in a self-consistent manner, analogous to the case[8] of an electron liquid.

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DERIVATION OF PHONON DISPERSION RELATIONS FROM ELECTRONIC STATES IN INSULATORS

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The electronic contribution to the force constants of lattice vibrations in insulators is studied in a Green's-function formalism. Results of an application of the method to LiF are given where the one-electron spectrum has been treated in the tight-binding approximation.

During the last years a number of articles have been published on the calculation of phonon dispersion curves for metals.[1-5] In contrast to this only a few attempts have been made to treat insulators by taking the contribution of the electrons to the force constants explicitly into account.[6-9] The difficulties associated with an application of the Born-Oppenheimer approximation to insulators have, instead, been avoided by pointing out the formal equivalence between calculations using electronic states and phenomenological force-constant models.[10,11] Numerical calculations were so far based on these models.

This Letter proposes a systematic way for the derivation of the dispersion relations in the harmonic Born-Oppenheimer approximation and gives preliminary results for the application of the method to LiF.

According to Born and Huang[12] the electronic contribution to the harmonic interatomic force constants is given by

$$\varphi(jj') = \frac{d}{dR(j)}\frac{d}{dR(j')}\langle H_{\mathrm{el}}\rangle. \tag{1}$$

Here the index j comprises the number of the unit cell l, the number of a particular lattice particle in the cell s, and the direction in which this particle is displaced from equilibrium α. $d/dR(j)$ denotes the corresponding derivative, and H_{el} is the electronic Hamiltonian:

$$H_{\mathrm{el}} = \sum_i \left[\frac{\hbar^2}{2m}\frac{d^2}{d\vec{r}_i^{\,2}} + V(\vec{r}_i)\right] + \tfrac{1}{2}\sum_{i,j}{}' v(\vec{r}_i - \vec{r}_j).$$

The summation runs over all electrons and the term $i = j$ is excluded from the second sum. H_{el} depends on the lattice configuration through the electron-ion potential $V(\vec{r})$. The Coulomb interaction between the electrons is denoted as $v(\vec{r} - \vec{r}\,')$. The derivatives in formula (1) are to be taken at the equilibrium position of the ions.

We specify the average over the electronic Hamiltonian to be performed with the ground-state electronic wave function. Thus, temperature dependence is not included in the treatment although there is no principal objection to a generalization of the formulas using temperature-dependent Green's functions.

With the aid of the Hellman-Feynman theorem Eq. (1) can be rewritten as

$$\varphi(jj') = [d/dR(j)]\langle dH_{\mathrm{el}}/dR(j')\rangle. \tag{2}$$

Introducing the electronic Green's function by

$$G(12) = (-i)\langle T[\psi(1)\psi^\dagger(2)]\rangle,$$

where the variables 1 and 2 stand for space and time coordinates of the respective particles, T means time ordering of the quantities in the brackets, and $\psi(1)$ and $\psi^\dagger(2)$ are fermion annihilation and creation operators in the Heisenberg picture, we get from Eq. (2)

$$\varphi(jj') = (-i)\int d\tau \left[\frac{dG(11^+)}{dR(j)}\frac{dH_{\mathrm{el}}}{dR(j')} + G(11^+)\frac{d}{dR(j)}\frac{d}{dR(j')}H_{\mathrm{el}}\right]. \tag{3}$$

Here the symbol 1^+ means that an infinitesimal time argument $\epsilon > 0$ has been added to t_1 to insure the correct order of the field operators in the Green's function.