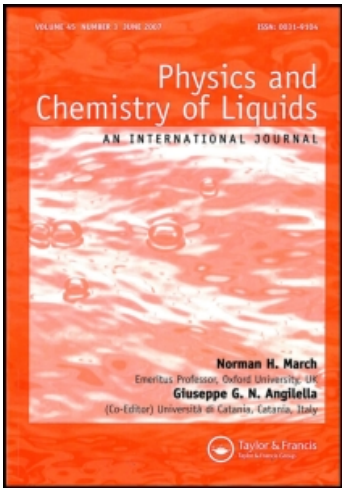

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LETTER
Collective Modes and Liquid Structure Theory of Metallic Rb

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The basic shape of the Hubbard-Beeby type theory of the dispersion relation of the collective excitations in classical liquids has been examined using the existing molecular dynamics data for liquid rubidium. The MD data put constraints on the form of the function $Q(k, O)$ appearing in the theory. The observations made here are expected to be useful for the development of a theory of collective excitation in liquid metals.

KEY WORDS: Density fluctuations, direct correlation function.

As demonstrated in the work of Copley and Rowe,[1] and subsequently by Rahman,[2] density fluctuations propagate very differently in liquid metal Rb on the one hand, and liquid Ar on the other.

When collective modes are a dominant physical feature of the liquid, as in Rb, the theory of the dynamical structure factor $S(k, \omega)$ due to Hubbard and Beeby[3] seems still to offer a useful starting point, in spite of known quantitative difficulties.[4,5] In this theory,[3] the static structure factor takes the form

$$S(k) = \frac{k^2}{\beta M} \frac{Q(k, O)}{1 + \omega_k^2 Q(k, O)}; \beta = (k_B T)^{-1}. \tag{1}$$

The present work is concerned with the basic shape of the theory expressed in Eqn. (1), not the quantitative form of the Hubbard-Beeby theory of the dispersion relation ω_k of the collective mode, and the function $Q(k, O)$, which is related to the dynamics of self motion in this theory.[3,6]

Let us now rewrite Eqn. (1) in terms of the direct correlation function $c(r)$, with Fourier transform $c(k)$ related to $S(k)$ by

$$c(k) = \frac{S(k) - 1}{S(k)} \tag{2}$$

The resulting form for $c(k)$ is then

$$c(k) = 1 - \frac{\beta M}{k^2 Q} - \frac{\omega_k^2}{k^2} \beta M \tag{3}$$

which follows directly from Eqns. (1) and (2). Taking $c(k)$ from the molecular dynamical $S(k)$ of Rahman[2] for liquid Rb, and ω_k from his computer simulation, we show in Figure 1, a plot of $c(k)$ and of $1 - \omega_k^2\ \beta M/k^2$ separately. Figure 2 shows the difference between the two curves in Figure 1, which according to Eqn. (3) would yield the quantity $\beta M/k^2 Q(k, O)$.

It is to be noted that in a Feynman-like theory[7] of the collective mode, for which $\omega_k^2 = k^2/\beta M S(k)$, the term $\beta M/k^2 Q$ in Eqn. (3) would be put equal to zero. In the Hubbard-Beeby theory $\beta M/k^2 Q(k, O)$ is completely determined by the dynamics of self motion. These values are found to be very different from the plot in Figure 2 extracted from computer experiment. The extracted values of $\beta M/k^2 Q(k, O)$ in Figure 2 should be useful for proposing a model for $Q(k, O)$.

In conclusion, it may be fruitful in the future to compare the shape of the Hubbard-Beeby-like theory, most usefully expressed in Eqn. (3), with that proposed by March and Senatore[8] for a liquid like Argon, in which, in contrast to Eqn. (3), an r-space decomposition is made of $c(r)$:

$$c(r) = c_\rho(r) + c_c(r) \tag{4}$$

Here, March and Senatore[8] propose the form for the potential $\phi(r)$ contribution

$$c_\rho(r) = -\frac{\phi(r)}{k_\beta T}\left\{\frac{1}{6\rho r^2}\frac{\partial^2}{\partial\rho\partial r}[\rho^2 r^3 g(r, \rho)]\right\} \tag{5}$$

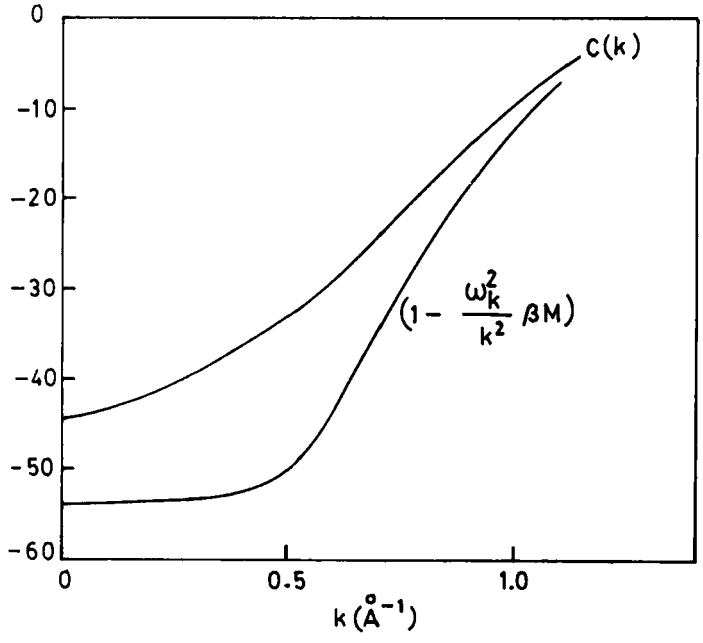

Figure 1 Variation of $c(k)$ and $1 - (\omega_k^2/k^2)\beta M$ with k.

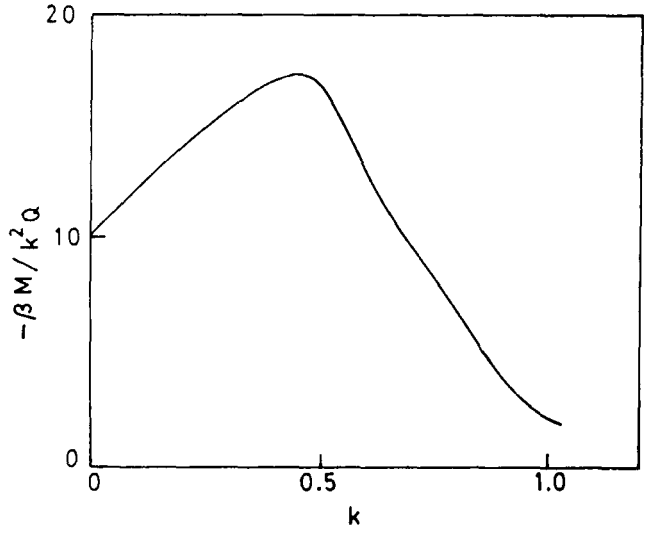

Figure 2 Variation of the difference between the two curves in Figure 1, i.e. $-\beta M/k^2Q$ (according to Eqn. 3) with k.

with density-independent pair potential $\phi(r)$ and corresponding pair correlation function $g(r, \rho)$. Then, to satisfy thermodynamic consistency, one must choose

$$\int c_c(r)d\mathbf{r} = O. \tag{6}$$

To date, no complete theory of $c_c(r)$ exists for argon.

Paralleling the above decomposition, one could rewrite Eqn. (3), appropriate to liquid Rb with a well-defined collective mode, as

$$c(k) = 1 - \frac{\beta M}{k^2 Q} - \frac{\omega_k^2}{k^2}\frac{\gamma}{v_s^2 S(O)} \tag{7}$$

using $S(O) = \rho k_B T K_T$. Clearly then, since it follows immediately from Eqn. (2) that $c(O) = 1 - 1/S(O)$ one can rewrite Eqn. (7) as

$$\lim_{k\to O} c(k) = 1 - \frac{1}{S(O)} - \frac{\beta M}{(k^2Q)_{k\to O}} - \left(\frac{\omega_k^2(\gamma - 1)}{k^2 v_s^2 S(O)}\right)_{k\to O} \tag{8}$$

If one assumes $\omega_k^2/k^2 \to v_s^2$, the square of the velocity of sound, in the long wavelength limit (see, however, Ref. 1), then Eqn. (8) would yield, from thermodynamic consistency

$$\frac{\beta M}{(k^2Q)_{k\to O}} = -\frac{(\gamma - 1)}{S(O)} \tag{9}$$

with $\gamma = c_p/c_v$, the specific heat ratio. One would not expect an approximate theory such as that of Hubbard and Beeby[3] to satisfy Eqn. (9). Since Q in that theory is

related to dynamics of self motion, as already emphasized, one might expect qualitatively that eqn. (9) implies a relation for liquid metals between self diffusion coefficient D and structure factor $S(O)$. Such a type of relation is indeed suggested by the work of Brown and March[9] which, however involves the Debye frequencies at the melting temperature, where their arguments are directly applicable.

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