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CONTRIBUTION OF VAN DER WAALS FORCES TO THE FORM FACTOR OF A LIQUID

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The contribution of van der Waals forces to the form factor of a liquid is found on the basis of the general macroscopic theory of the forces. The formula for this contribution involves the dielectric permittivity of the liquid, and is valid for all values of the wave vector k that are small in comparison with the inverse interatomic distance 1/a. It is shown that the van der Waals forces in liquid helium lead to the appearance of a singular term of the type μk^3 in the phonon dispersion law. The value of the coefficient μ is estimated.

IN this research, the contribution which the long-range van der Waals forces make to the correlation functions of the molecules of a liquid (the liquid form factor) is calculated. This question has previously been treated on the basis of microscopic theory.[1-5] It has been assumed that the atoms of the liquid interact through a pair van der Waals potential. Such an assumption generally does not have a basis, in fact, since the van der Waals forces in a liquid do not have a pair character. Below, we carry out the calculation on the basis of the general macroscopic theory of such forces without any additional assumptions.[6] The resultant formulas will be suitable for any relation between k and the characteristic wavelength λ_0 in the spectrum of the liquid.

The form factor of the liquid S(k) is determined by the formula

$$S(k)=\frac{1}{\bar{n}}\int e^{i(\mathbf{k},\,\mathbf{r}-\mathbf{r}')}\langle\delta n(\mathbf{r})\,\delta n(\mathbf{r}')\rangle\, d^3(r-r'), \tag{1}$$

where $\bar{n}$ is the mean number of atoms of the liquid per unit volume, δn the deviation of this number from its mean value. Averaging is carried out over the state of the liquid with given temperature and pressure. As is known, S(k) is determined experimentally in experiments on x-ray or neutron scattering in the liquid (see, for example,[7]). At the present time, the accuracy of the experiment has been so improved that one can expect a detailed study of S(k) for small k, i.e., in the case

$$ka\ll 1, \tag{2}$$

where a is the interatomic distance in the liquid. The theory to be set forth will be suitable under precisely such conditions.

For the calculation of S(k), we use its connection with the second variational derivative of the free energy F with respect to the density of atoms n. We represent ΔF in the form

$$\Delta F=\frac{1}{2V}\int\varphi(\mathbf{r}-\mathbf{r}')\,\delta n(\mathbf{r})\,\delta n(\mathbf{r}')\,d^3r\,d^3r'. \tag{3}$$

Then S(k) is expressed in terms of the Fourier component φ (see, for example,[8]):

$$S(k)=\frac{T}{\bar{n}\varphi(k)},\qquad \varphi(k)=\int e^{-i\mathbf{k}\mathbf{r}}\varphi(\mathbf{r})\,d^3r. \tag{4}$$

Thus, our problem consists of the calculation of the contribution of the van der Waals forces in $\varphi(k)$. Of course, the principal contribution to $\varphi(k)$ is made by the short-range forces. The possibility of the separation of the comparatively small contribution from the van der Waals forces is connected with another character of the dependence of this contribution on k. If we represent $\varphi(k)$ in the form

$$\varphi=\varphi_1+\varphi_2,$$

where φ_1 and φ_2 are determined by the contributions of the short-range and long-range forces, then $\varphi_1=\varphi_1(ka)$ and $\varphi_2=\varphi_2(k\lambda_0)$. Therefore, for the condition (2), φ_1 can be represented in the form

$$\varphi_1=\alpha+\beta k^2,\qquad \alpha=\frac{1}{\bar{n}}\left(\frac{\partial p}{\partial n}\right)_T.$$

In this region, the function φ_2 has a complicated and generally a singular dependence on k, for under the condition (2) the parameter $k\lambda_0$ can be larger or smaller than unity.

We proceed to the calculation of φ_2. For this purpose, we make use of the formula obtained in[9] for the variation of F with respect with the dielectric permittivity of the medium, ϵ:

$$\Delta F=-\frac{T}{4\pi}\sum_{m=0}^{\infty}{}'\,\omega_m{}^2\int D_{ii}(\mathbf{r},\mathbf{r};\omega_m)\,\delta\varepsilon(\mathbf{r},i\omega_m)\,d^3r, \tag{5}$$

where $\omega_m=2\pi mT$, m = 0, 1, 2, ..., and D_{ik} is the "Matsubara" Green's function, which satisfies the equation

$$\left\{\varepsilon(\mathbf{r}_1 i\omega_m)\,\omega_m{}^2\delta_{ie}-\delta_{ie}\frac{\partial^2}{\partial x_p{}^2}+\frac{\partial^2}{\partial x_i\partial x_e}\right\}D_{ep}(\mathbf{r}_1\mathbf{r}_2,\omega_m)=-4\pi\delta(\mathbf{r}_1-\mathbf{r}_2)\,\delta_{ip}. \tag{6}$$

It is seen from (6) that finding the second variation of F reduces to the variation of D_{ii} with respect to ϵ. From (6) we get the equation for δD_{ii}:

$$\begin{gathered}\left\{\frac{\partial^2}{\partial x_i\partial x_e}-\delta_{ie}\frac{\partial^2}{\partial x_p{}^2}+\varepsilon(\mathbf{r},i\omega_m)\,\omega_m{}^2\delta_{ie}\right\}\delta D_{ep}(\mathbf{r}_1,\mathbf{r}_2;\omega_p)\\ =-\delta\varepsilon(\mathbf{r},i\omega_m)\,\omega_m{}^2\delta_{ie}D_{ep}(\mathbf{r}_1-\mathbf{r}_2,\omega_m).\end{gathered} \tag{7}$$

This equation is easily solved with account of the fact that D_{ik}, by virtue of (6), is the Green's function for (7). As a result,

$$\delta D_{ee}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{4\pi}\omega_p{}^2\int\delta\varepsilon(\mathbf{r}_3)\,D_{ik}(\mathbf{r}_3-\mathbf{r}_2)\,D_{ik}(\mathbf{r}_3-\mathbf{r}_1)\,d^3r_3. \tag{8}$$

Setting

$$\delta\varepsilon(i\omega_m,\mathbf{r})=\frac{\partial\varepsilon(i\omega_m)}{\partial n}\,\delta n(\mathbf{r}) \tag{9}$$

and substituting (8) and (9) in (5), we obtain

$$\Delta F = \frac{T}{4\pi}\sum_{m=0}^{\infty}\int \omega_m^4 D_{ie}^2(\mathbf{r}-\mathbf{r}')\left(\frac{\partial\varepsilon}{\partial n}\right)^2 \delta n(\mathbf{r})\,\delta n(\mathbf{r}')\,d^3r\,d^3r'. \quad (10)$$

Expressing D_{ik} in the form of a Fourier integral, we directly obtain the expression for the van der Waals part of $\varphi(k)$:

$$\varphi_2(k) = \frac{T}{2(2\pi)^3}\sum_{m=0}^{\infty}\omega_m^4\int D_{ie}(\mathbf{p})D_{ie}(\mathbf{p}-\mathbf{k})\left(\frac{\partial\varepsilon}{\partial n}\right)^2 d^3p. \quad (11)$$

In the derivation of (4), we assumed that the temperature T is sufficiently high that the density fluctuations can be assumed to be classical. On the other hand, the fluctuations of the electromagnetic field will be assumed to be zero, i.e., purely quantum in nature. Satisfaction of both these conditions is guaranteed by the inequalities

$$\hbar ku \ll T \ll \hbar kc \quad (12)$$

(u is the velocity of sound in the liquid, c the velocity of light). In this case, we can go from summation over ω to integration. We then obtain

$$\varphi_2(k) = \frac{1}{2(2\pi)^4}\int_0^{\infty} d\omega\int \omega^4 D_{ie}(\mathbf{p})D_{ie}(\mathbf{p}-\mathbf{k})\left[\frac{\partial\varepsilon(i\omega)}{\partial n}\right]^2 d^3p. \quad (13)$$

Here

$$D_{ie}(p) = -\frac{4\pi}{\varepsilon\omega^2+p^2}\left(\delta_{ie}+\frac{p_ip_e}{\varepsilon\omega^2}\right). \quad (14)$$

We compute the integral over d^3p. From the formal point of view, this integral diverges. However, this is connected with the fact that the expression (13) holds only for $pa \ll 1$. In actuality, the integrand falls off for large p, because of the spatial dispersion of ϵ, for example. This indicates the correctness of the method of taking the integral.

First of all, we note that, after integrating over the directions of **p**, the integrand becomes an even function of $|\mathbf{p}|$, so that integration with respect to $|\mathbf{p}|$ can be carried out from $-\infty$ to $+\infty$. The falling off of the integrand outside the region of applicability of (13), already noted above, allows us to close the contour of integration in the plane of the complex variable, so that integration with respect to dp reduces to taking the residues at the poles of the integrand (such a method of calculation of an integral similar to (13), was used in[10]).

The final result has the form

$$\varphi_2(k) = \int_0^{\infty}\frac{d\omega}{\sqrt{\varepsilon}}\left(\frac{\partial\varepsilon}{\partial n}\right)^2\omega^3 g\left(\frac{k}{\sqrt{\varepsilon}\,\omega}\right). \quad (15)$$

Here $\epsilon = \epsilon(i\omega)$ and

$$g(x) = \pi\left[\left(\frac{2}{x}+x+\frac{x^3}{4}\right)\left(\operatorname{arctg}x-\operatorname{arctg}\frac{2}{x}\right)\right. \quad (16)$$

$$\left.+\left(\frac{2}{x}+2x+\frac{3}{16}x+\frac{x^5}{8}\right)\frac{1}{1+\frac{x^2}{2}}\operatorname{arctg}\frac{2}{x}\left(1+\frac{x^2}{2}\right)+x^2\right]-2\pi.$$

Correspondingly, with the necessary accuracy,

$$S(k) \approx \frac{T}{\bar{n}\alpha}\left(1-\frac{\beta}{\alpha}k^2-\frac{\varphi_2}{\alpha}\right). \quad (17)$$

In the limit of large k, $k\lambda_0 \gg 1$,

$$\varphi_2(k) \approx \frac{\pi^2}{4}\int_0\frac{d\omega}{\sqrt{\varepsilon}}\left(\frac{\partial\varepsilon}{\partial n}\right)^2\frac{k^3}{\varepsilon^{3/2}}. \quad (18)$$

For small k, $k\lambda_0 \ll 1$,

$$\varphi_2(k) \approx \pi\int_0^{\infty}\frac{d\omega}{\sqrt{\varepsilon}}\left(\frac{\partial\varepsilon}{\partial n}\right)^2\left(\frac{11}{6}\frac{k^2\omega}{\varepsilon}+\frac{23}{120}\frac{k^4}{\varepsilon^2\omega}\right). \quad (19)$$

The integral with respect to $d\omega$ in the second term of (19) diverges logarithmically and it must be cut off at $\omega \sim 1/k$. As a result, we get a singular term of the form

$$\varphi_2(k) = \pi\frac{1}{\varepsilon_0^{5/2}}\left(\frac{\partial\varepsilon_0}{\partial n}\right)^2\frac{23}{120}k^4\ln\frac{1}{k}, \quad (20)$$

where $\epsilon_0 = \epsilon(0)$ is the static value of the dielectric permittivity. If we replace $\partial\epsilon/\partial n$ by $\kappa\,(i\omega)/4\pi$ in (18) and (19) (κ is the dielectric polarizability of an isolated atom) and replace ϵ in the denominator by unity, then these expressions go over into the expression for the Fourier components of the ordinary formulas of London and Casimir-Polder for the atomic interaction potential. Then the formulas for $\varphi(k)$ become identical with the formulas of[1-5]. We see that the deviation of ϵ from unity and of $\partial\epsilon/\partial n$ from $\kappa/4$ are measures of the nonadditivity of the van der Waals interactions in a liquid. In other words, the formulas obtained in[1-5] are strictly valid only for a gas. We also note that Eqs. (18) and (20) are formally identical with the formulas for the interaction of foreign particles dissolved in a liquid.[11] This identity appears to us to be somewhat accidental, since the atoms of the liquid cannot be regarded as foreign particles.

Equations (15) and (16) express the van der Waals form factor in general form in terms of the dielectric permittivity of the liquid (the dielectric constant on the imaginary axis is expressed in well-known fashion by the imaginary part of ϵ for real frequencies[6]).

It is easy to verify that the integrand of (15) has no singularities in the right half-plane of ω. This allows us to move the contour of integration and make it coincide with the lower half of the imaginary axis. We then set $i\omega = \omega'$, so that the answer is expressed in terms of the value of ϵ for real ω.

At the present time, the dependence of ϵ and $\partial\epsilon/\partial n$ on ω is unknown in the entire range of frequencies with sufficient accuracy for any one liquid. It would therefore be of great interest to determine $\varphi_2(k)$ experimentally, which would allow us to draw definite conclusions on the form of $\epsilon(\omega)$.[1]

Let us make a comparative estimate of the van der Waals and "short-range" parts of φ. Of course, we are dealing with the terms that depend on k. The contribution of the van der Waals forces to the isothermal compressibility α is negligible.[2] A simple estimate, based on dimensional considerations, shows that

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[1] Formulas (15) and (16) allow us, in principle, to express the value of $\sigma\epsilon(i\omega)/\partial n$ in terms of the quantity $\omega\sqrt{\epsilon(i\omega)}$ if the function $\varphi_2(k)$ is known. Actually, (15) can be regarded as an integral equation for the determination of $\partial\epsilon/\partial_n$ as a function of $\omega\sqrt{\epsilon}$. This equation can be solved explicitly with the help of a Mellin transformation. If a specific dependence of ϵ on n is given, for example, the "gas" dependence ($\epsilon-1 \sim n$) or the dependence according to the Clausius-Mosotti formula, then we can determine the form of the function $\epsilon(i\omega)$ from the dependence of $\partial\epsilon(i\omega\sqrt{\epsilon(i\omega)})/\partial n$.

[2] The part of $\varphi_2(k)$ that does not depend on k^2 diverges logarithmically, and we have already taken it into account in (15) by requiring that $\varphi_2(k) \to 0$ as $k \to 0$.

$$\beta k^2 \sim \frac{\Theta}{a} k^2, \tag{21}$$

where Θ is the Debye temperature of the liquid in energy units, and a is a length of the order of the interatomic distance in the liquid. On the other hand, φ_2 is of the order

$$\varphi_2 \sim \begin{cases} \hbar\omega_0 k^3, & k\lambda_0 \gg 1, \\ \hbar\omega_0 k^2/\lambda_0, & k\lambda_0 \ll 1, \end{cases} \tag{22}$$

where ω_0 is the characteristic frequency of the electron spectrum of the liquid. It is seen from (22) that for $k\lambda_0 \gg 1$ the van der Waals contribution exceeds the short-range contribution for the condition

$$ka \gg \Theta / \hbar\omega_0. \tag{23}$$

Since $\hbar\omega_0 \gg \Theta$, the condition (23) is compatible with (2) (the characteristic value is $\hbar\omega_0 \sim 10$ eV, and $\Theta \sim 0.1$ V). On the other hand, for small k ($k\lambda_0 \ll 1$), the short-range term $\Theta k^2/a$ and the long-range term $\hbar\omega_0 k^2/\lambda_0$ are generally of the same order, although the possibility is not excluded that the van der Waals term can be large in a liquid consisting of heavy atoms. In the opposite case, only the singular term of order $k^4 \ln k$ could be determined from the experimental data.

The presence of terms in $\varphi(k)$ that are singular in k^2 leads to the appearance of the same terms in the law of sound dispersion $\omega(k)$. We discuss this question as applied to liquid He^4 at T = 0. The Fourier component of the van der Waals interaction potential of helium atoms is equal to[12]

$$U(k) = -\frac{\pi^2}{12} U_0 R^3 (kR)^3, \quad k\lambda_0 \gg 1, \tag{24}$$

where $U_0 = 36°K$ and R = 2.6 Å. Since, from the electrodynamic point of view, helium is close to a gas, exactly such a term will be contained in $\varphi(k)$. On the other hand, the law of sound dispersion for T = 0 and sufficiently small k has the form[13]

$$\omega^2(k) = k^2 \varphi(k) \frac{\bar{n}}{m} U. \tag{25}$$

The expression (24) then leads to the appearance of an anomalous term $\sim k^3$ in the sound velocity u. Normally, expansion of u(k) is carried out in powers of k^2. We have already mentioned that the term $\sim k^3$ in the region $k\lambda_0 \gg 1$ can exceed the term $\sim k^2$. Further, there is evidence that the term $\sim k^2$ in helium is especially and anomalously small (see[14,15]). Therefore, for not too small k, the formula

$$u = \frac{\omega}{k} \approx u_0 \left[1 - \frac{1}{2} \mu (kR)^3\right],$$

should hold, where $\mu = \pi^2 \rho U_0 R^3 / 12 m^2 \approx 0.42$, $u_0 \approx 239$ m/sec; $\rho = 0.145$ g/cm^3 is the helium density.

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