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THE BEHAVIOR OF THE STRUCTURE FACTOR OF A CLASSICAL LIQUID WITH SMALL WAVE NUMBERS

I. Z. FISHER

Odessa State University

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The analytical properties of the structure factor $S(\kappa)$ as $\kappa \to 0$ are discussed for a simple classical liquid far from the critical point. The factor is considered to be a function of the real variable $\kappa = |\kappa|$. It is shown that $S(\kappa)$ has two types of non-analytic parts, a logarithmic contribution with leading term $\sim \kappa^4 \ln \kappa$ and a term which is discontinuous in the fifth derivative and possesses a leading term $\sim |\kappa|^5$. Some initial terms of the asymptotic series describing both non-regular parts of the structure factor are found explicitly.

1. INTRODUCTION

THE structure factor of a liquid or dense gas $S(\kappa)$ is the most important characteristic correlating the structure and properties of these systems. However, almost all our knowledge of $S(\kappa)$ at the present time is purely empirical, has low accuracy, and is limited to small regions of values of κ. An important theoretical achievement has been the proof in [1] that $S(\kappa)$ is nonanalytic as a function of the real variable κ at the points $\kappa = 0$ and has the expansion

$$S(\varkappa) = a_0 + a_2\varkappa^2 + a_3|\varkappa|^3 + \ldots \tag{1}$$

near this point, with discontinuous third derivative. Such a character of the non-analyticity of $S(\kappa)$ was obtained in connection with the falling off, at large distances, of the pair dispersion forces between particles, according to the law r^{-6}. The behavior of $S(\kappa)$ near $\kappa = 0$ would be different for a different fall-off of the intermolecular forces.

In the present work, we want to obtain a more realistic and more exact estimate for the asymptotic behavior of the pair potential of intermolecular forces $\Phi(r)$ and the radial distribution function $g(r)$ as $r \to \infty$ for a classical liquid or dense gas and, in this connection, to re-examine the question of the character of the non-analyticity of the structure factor $S(\kappa)$ as $\kappa \to 0$. It will be shown that the principal singularities in $S(\kappa)$ are logarithmic, of the type $\kappa^4 \ln \kappa$ in place of $|\kappa|^3$ in [1]. The basis for such a review of the results of [1] is the well-known fact[2] that the actual asymptote for the interparticle pair potential, found with account of the finite propagation velocity of the electromagnetic interactions, has the form $\Phi(r) \sim -r^{-7}$ in place of the asymptote $\Phi(r) \sim -r^{-6}$ used in [1], the latter corresponding to the electrostatic approximation.

We shall consider a classical system with a Hamiltonian that depends strictly only on the central pair interparticle interactions

$$H = \sum_{j=1}^{N} \frac{\mathbf{p}_j^2}{2m} + \frac{1}{2}\sum_{j\neq l} \Phi(|\mathbf{r}_j - \mathbf{r}_l|) \tag{2}$$

in the limit $N \to \infty$. The connection between the asymptotic behavior of $\Phi(r)$ and the radial distribution function $g(r)$ as $r \to \infty$ is given by the exact relation found by Kuni[3]

$$g(r) - 1 = -kT(\partial n/\partial P)_T{}^2\Phi(r) + O([\Phi(r)]^2), \tag{3}$$

where n is the mean particle-number density and P is the pressure. The relation (3) was obtained less rigorously and later also used in [1]. The functions $g(r)$ and $S(\kappa)$ are connected in turn with the well known relation (see [4])

$$\varkappa(S(\varkappa) - 1) = 4\pi n \int_0^\infty r(g(r) - 1)\sin(\varkappa r)\,dr. \tag{4}$$

2. THE ASYMPTOTE OF THE PAIR POTENTIAL AND OF THE RADIAL DISTRIBUTION FUNCTION

We shall establish the form of the potential $\Phi(r)$ at large distances by following the discussions of [5]. An inessential difference will consist of allowance for a larger number of terms in the asymptotic expansion of $\Phi(r)$. We shall start out from the exact formula obtained in [5] for the force of attraction between two macroscopic media separated by a plane parallel gap of width l, which follows from the quantum theory of electromagnetic fluctuations (see also [6, 7]). Let both media be the same and let $\epsilon(\omega)$ be their dielectric permittivity at the frequency ω. Then at distances $l \gg \hbar c/I$, where I is the ionization potential of the molecule, this force is equal to

$$F(l) = -\frac{\hbar c}{32\pi^2 l^4}\int_0^\infty x^3\,dx \int_1^\infty \left\{\left[\left(\frac{s+p}{s-p}\right)^2 e^x - 1\right]^{-1} + \left[\left(\frac{s+p\varepsilon}{s-p\varepsilon}\right)^2 e^x - 1\right]^{-1}\right\}\frac{dp}{p^2}, \tag{5}$$

where

$$s = \sqrt{\varepsilon - 1 + p^2}, \qquad \varepsilon = \varepsilon(icx/2lp). \tag{6}$$

If the two media are gaseous, then we have

$$\varepsilon(\omega) = 1 + 4\pi n a(\omega) + O(n^2), \tag{7}$$

where $a(\omega)$ is the molecular polarizability at the frequency ω and $\epsilon - 1$ is small. Then simple transformations reduce Eq. (5) to the form

$$F(l) = -\frac{\hbar c n^2}{16 l^4} \int_0 x^3 e^{-x}\, dx \int_1^\infty \frac{1-2p^2+2p^4}{p^6} \left[a\left(i\frac{cx}{2lp} \right) \right]^2 dp + O(n^3). \tag{8}$$

We are interested in the value of $a(i\omega)$ as $\omega \to 0$. We denote by $\alpha(\omega)$ and $\beta(\omega)$ the real and imaginary parts of the molecular polarizability; $\alpha(\omega)$ is even and $\beta(\omega)$ odd in ω. Then, for small ω, we have

$$\begin{aligned} a(i\omega) &= \alpha(i\omega) + i\beta(i\omega) \\ &= \alpha(0) - \omega\beta'(0) - \frac{\omega^2}{2}\alpha''(0) + \frac{\omega^3}{6}\beta'''(0) + \frac{\omega^4}{24}\alpha^{\mathrm{IV}}(0) + \ldots . \end{aligned} \tag{9}$$

Substitution in (8), after integration, leads to the asymptotic form

$$F(l) = -\frac{\hbar c n^2}{8 l^4} \left\{ \frac{23}{5}\alpha_0 + A_1 \frac{c}{l} + A_2 \frac{c^2}{l^2} + \ldots \right\} + O(n^3), \tag{10}$$

where

$$\begin{aligned} &A_1 = -8\alpha_0\beta_0', \quad A_2 = -{}^{43}/_{7}(\alpha_0\alpha_0'' - \beta_0'^2), \\ &A_3 = {}^{35}/_{8}(\alpha_0\beta_0''' + 3\alpha_0''\beta_0'), \ldots \end{aligned} \tag{11}$$

and for brevity, we set $\alpha(0) = \alpha_0$, $\beta'(0) = \beta_0'$, etc.

On the other hand, for a gaseous medium with intermolecular pair potential $\Phi(r)$, the form $F(l)$ can be computed directly. Expanding, for large distances,

$$\Phi(r) = -\frac{1}{r^m}\left(B_0 + \frac{B_1}{r} + \frac{B_2}{r^2} + \ldots \right), \quad m > 3, \tag{12}$$

we get after elementary calculation, for large l,

$$F(l) = -\frac{2\pi n^2}{l^{m-3}} \sum_{k \geqslant 0} \frac{B_k}{(m-3+k)(m-2+k) l^k} + O(n^3). \tag{13}$$

Comparing (13) and (10), we find that $m = 7$,

$$B_k = \frac{\hbar c^{k+1}}{16\pi}(4+k)(5+k)A_k. \tag{14}$$

Thus, we have for the asymptote of the pair potential at large distances,

$$\Phi(r) = -\frac{6\hbar c}{\pi r^7}\left\{ \frac{23}{24}\alpha_0^2 + \sum_{k \geqslant 1} \bar{B}_k \left(\frac{c}{r} \right)^k \right\}, \quad r \gg \frac{\hbar c}{I}, \tag{15}$$

with the corresponding values of the coefficients:

$$\begin{gathered} \bar{B}_1 = -{}^{5}/_{2}\alpha_0\beta_0', \ \bar{B}_2 = -{}^{43}/_{16}(\alpha_0\alpha_0'' - \beta_0'^2), \ \bar{B}_3 = {}^{245}/_{96}(\alpha_0\beta_0''' + 3\alpha_0''\beta_0'), \\ \bar{B}_4 = {}^{71}/_{16}(\alpha_0\alpha_0^{\mathrm{IV}} + 3\alpha_0''^2 - 4\beta_0'\beta_0'''), \\ \bar{B}_5 = -{}^{231}/_{64}(\alpha_0\beta_0^{\mathrm{V}} + 10\alpha_0''\beta_0''' - 5\alpha_0^{\mathrm{IV}}\beta_0') \\ \bar{B}_6 = -{}^{535}/_{384}(\alpha_0\alpha_0^{\mathrm{VI}} + 15\alpha_0''\alpha_0^{\mathrm{IV}} - 6\beta_0'\beta_0^{\mathrm{V}} - 10\beta_0'''^2) \ \text{etc.} \end{gathered} \tag{16}$$

The zero term in (15) corresponds exactly to the result of [2] and had been obtained in [5] with the aid of the expression for the force $F(l)$. All the remaining terms in (15) correspond to further approximations of the asymptote of $\Phi(r)$. It is seen that all the odd terms in (15) disappear if we neglect the dissipative part of the molecular polarizability $\beta(\omega)$. For monatomic molecules or for other molecules that are sufficiently simple, the contribution from these terms to the asymptote of $\Phi(r)$ is very small.

Using the expression (3), it is now easy to establish the asymptotic expression for the radial distribution function at large distances:

$$g(r) - 1 = \frac{6kT}{\pi}\left(\frac{\partial n}{\partial P} \right)_T^2 \frac{\hbar c}{r^7}\left\{ \frac{23}{24}\alpha_0 + \sum_{k=1}^{k=6} \bar{B}_k \left(\frac{c}{r} \right)^k \right\} + O\left(\frac{1}{r^{14}} \right). \tag{17}$$

In actuality, in addition to the power-series part of the asymptote of $g(r) - 1$ described here, there is also an exponentially decaying part.[4] Contributions decaying exponentially with increase in l should also be added to (8) (see [5,6]). However, for our purposes, these refinements are unimportant. The applicability of the estimate (17) as well as of the estimate (3) is limited only by the condition of being far from the critical point of the liquid, where $(\partial n/\partial P)_T \to \infty$.

3. THE BEHAVIOR OF THE STRUCTURE FACTOR NEAR $\kappa = 0$

From Eq. (4) for the structure factor, we can directly establish the fact that the function $S(\kappa)$ itself and its first three derivatives exist at the point $\kappa = 0$, are continuous, and are respectively equal to

$$\begin{gathered} S(0) = 1 + 4\pi n \int_0^\infty r^2 (g(r) - 1)\, dr = nkT\beta_T, \\ S''(0) = -\frac{4\pi n}{3} \int_0^\infty r^4 (g(r) - 1)\, dr, \quad S'(0) = S'''(0) = 0, \end{gathered} \tag{18}$$

where β_T is the isothermal compressibility of the system (see [8]). However, the fourth derivative at the point $\kappa = 0$ and all higher derivatives do not exist as a consequence of the slow decrease in the function $g(r) - 1$ with increase in r, in accord with (17). Let $\varphi(r)$ be some arbitrary continuous function, possessing only the property that both of the integrals on the right side of Eq. (19) below exist. Then, in place of Eq. (4) for the structure factor, we can write the identically equal expression

$$\begin{aligned} \varkappa(S(\varkappa) - 1) &= nkT\left(\frac{\partial n}{\partial P} \right)_T^2 \hbar c \int_0^\infty \varphi(r) \sin(\varkappa r)\, dr \\ &+ 4\pi n \int_0^\infty \left\{ r(g(r) - 1) - \frac{kT}{4\pi}\left(\frac{\partial n}{\partial P} \right)_T^2 \hbar c \varphi(r) \right\} \sin(\varkappa r)\, dr. \end{aligned} \tag{19}$$

The integrand of the second integral behaves as

$$\frac{kT}{4\pi}\left(\frac{\partial n}{\partial P} \right)_T^2 \hbar c \left\{ \frac{23\alpha_0^2}{r^6} + \frac{24}{r^6} \sum_{k \geqslant 1} \bar{B}_k \left(\frac{c}{r} \right)^k - \varphi(r) \right\} \sin(\varkappa r). \tag{20}$$

for large values of r. Therefore, it is not difficult to select the function $\varphi(r)$ so as to compensate any number of higher terms in (20) and to keep the possibility of a sufficiently simple estimate of the first of the integrals in (19). Otherwise, $\varphi(r)$ can remain arbitrary.

As an example, we consider the function

$$\varphi(r) = \frac{23\alpha_0^2 r - 60c\alpha_0\beta_0'}{r(r_0^2 + r^2)^3} + \varphi_1(r), \tag{21}$$

where r_0 is some molecular length and $\varphi_1(r)$ a new arbitrary function, which falls off as $r \to \infty$ no slower than r^{-8}. It is easy to see that, for such a choice of $\varphi(r)$, the two principal terms in the asymptotic estimate (20) cancel one another. Therefore the second integral in (19) as a function of κ leads to regular contributions to $S(\kappa)$ up to the fifth derivative at the point $\kappa = 0$ inclusively. The possible nonregular contributions to the same order are then connected with the first integral in (19). Thus, one should estimate the principal nonregular terms for $\kappa = 0$ by the following integral:

$$\int_0^\infty \frac{23\alpha_0^2 r - 60c\alpha_0\beta_0'}{r(r_0^2 + r^2)^3} \sin(\varkappa r)\, dr. \tag{22}$$

For this case we consider two tabulated integrals:[8]

$$J_0=\int_0^\infty \frac{\sin(\varkappa r)}{r_0^2+r^2}\,dr=\frac{\varkappa}{2r_0|\varkappa|}\{e^{-|\varkappa|r_0}\,\mathrm{Ei}(|\varkappa|r_0)-e^{|\varkappa|r_0}\,\mathrm{Ei}(-|\varkappa|r_0\},\tag{23}$$

$$J_1=\int_0^\infty \frac{\sin(\varkappa r)}{r(r_0^2+r^2)}\,dr=\frac{\pi\varkappa}{2r_0^2|\varkappa|}(1-e^{-|\varkappa|r_0}).$$

Triple differentiation of each of these with respect to r_0 leads to the integrals that enter in (22). By separating the logarithmic terms from Ei ($\pm|\kappa|r_0$), we get, for small values of

$$J_0=-\frac{\varkappa^5}{120}\left(1+\frac{\varkappa^2r_0^2}{14}+\ldots\right)\ln(\gamma|\varkappa|r_0)$$
$$+\frac{\varkappa}{4r_0^4}\left(1-\frac{\varkappa^2r_0^2}{6}+\frac{2\varkappa^4r_0^4}{45}-\frac{4\varkappa^6r_0^6}{525}+\ldots\right),$$
$$J_1=\frac{3\pi\varkappa}{16r_0^5}\left(1-\frac{\varkappa^2r_0^2}{18}+\frac{\varkappa^4r_0^4}{120}-\frac{|\varkappa|^5r_0^5}{270}+\frac{\varkappa^6r_0^6}{1008}\ldots\right),\tag{24}$$

where $\gamma = e^C$, C being Euler's constant. It follows from (19)–(24) that the principal nonregular terms in $S(\kappa)$ at $\kappa = 0$ are equal to

$$nkT\left(\frac{\partial n}{\partial P}\right)_T^2\frac{\hbar c\varkappa^4}{120}(-23\alpha_0^2\ln(\gamma|\varkappa|r_0)+5\pi c\alpha_0\beta_0'|\varkappa|+\ldots).\tag{25}$$

By continuing the procedure of compensation of the successive terms in (20) with the help of integrals of the type

$$\int_0^\infty \frac{\sin(\varkappa r)}{(r_0^2+r^2)^n}\,dr,\quad \int_0^\infty \frac{\sin(\varkappa r)}{r(r_0^2+r^2)^n}\,dr,\tag{26}$$

we can obtain the nonregular terms in $S(\kappa)$ that follow after (25). Omitting the cumbersome calculations, we put down the final result. The function $S(\kappa)$ in the vicinity of the point $\kappa = 0$ can be represented in the form of a sum of three functions

$$S(\varkappa)=S_0(\varkappa)+S_1(\varkappa)+S_2(\varkappa).\tag{27}$$

The function $S_0(\kappa)$ is regular at the point $\kappa = 0$, is even, and has the expansion

$$S_0(\varkappa)=S(0)+{}^1\!/_2S''(0)\varkappa^2+A\varkappa^4+B\varkappa^6+\ldots\tag{28}$$

The first two coefficients are determined by (18), and the later terms are very complicated and we shall not write them down. The function $S_1(\kappa)$ has a logarithmic singularity in the fourth derivative at the point $\kappa = 0$, is even and its expansion is equal to

$$S_1(\varkappa)=-nkT\left(\frac{\partial n}{\partial P}\right)_T^2\frac{\hbar c}{120}\varkappa^4\ln(\gamma|\varkappa|r_0)$$
$$\times\left(23\alpha_0^2-\frac{4\bar{B}_2}{7}c^2\varkappa^2+\frac{\bar{B}_4}{126}c^4\varkappa^4-\frac{\bar{B}_6}{13860}c^6\varkappa^6+\ldots\right)\tag{29}$$

with coefficients $\bar{B}_{2n}$ from (16). Finally, the function $S_2(\kappa)$ has a continuous fifth derivative at the point $\kappa = 0$, is even and its expansion is

$$S_2(\varkappa)=-nkT\left(\frac{\partial n}{\partial P}\right)_T^2\frac{\pi\hbar c}{60}|\varkappa|^5\left(\bar{B}_1-\frac{\bar{B}_3}{56}c^2\varkappa^2+\frac{\bar{B}_5}{5040}c^4\varkappa^4-\ldots\right)\tag{30}$$

with coefficients $\bar{B}_{2n+1}$ from (16). It is seen that the auxiliary length r_0 introduced earlier falls out from the result as it should. Terms with ln (γr_0), which can be separated from $S_1(\kappa)$, are regular in κ and are exactly compensated with similar terms from $S_0(\kappa)$.

The appearance of a nonregular contribution $S_2(\kappa)$ in (26) is connected with the account of the dissipative part of the molecular polarizability $\beta(\omega)$. If we set $\bar{\beta}(\omega) \equiv 0$, then $S_2(\kappa)$ disappears and the coefficients $\bar{B}_{2n}$ in (16) are greatly simplified.

4. DISCUSSION OF RESULTS

The results of (27)–(30) are accurate for the model of a nonmetallic classical liquid far from the critical point that is generally accepted at the present time. The basis of this model is the assumption of the pair character of the intermolecular forces (1). The problem of the correctness of the results (27)–(30) for real liquids is unclear, inasmuch as there are no accurate data on the degree of suitability of this same model. In real simple liquids there exists a small impurity of triple and more complicated collective interactions;[9] however, their characteristic asymptote at large distances, with account of the retardation of the electromagnetic interactions and their contribution to the exact asymptote of the radial distribution function have not been studied. Here the fundamental problem is not whether there exists an appreciable collective contribution to the total energy of the system, but the extent to which this contribution can be assumed to be independent of the density of the system. In the same measure, that this independence exists, so our results remain valid even in the presence of collective interaction, inasmuch as the potential $\Phi(r)$ in (1) can be treated only as an effective pair potential without change in the discussions set down above. The situation remains unclear if the collective interactions depend appreciably on the density of the system.

The static structure factor $S(\kappa)$ is the zero moment in frequency of the more general dynamic formfactor $S(\kappa, \omega)$, which plays a fundamental role in the theory of scattering of slow neutrons by simple liquids. If we introduce the moments of all orders

$$\mu_n(\varkappa)=\int_{-\infty}^{\infty}\omega^nS(\varkappa,\omega)\,d\omega,\tag{31}$$

then for the classical liquid,

$$\mu_0(\varkappa)=S(\varkappa),\quad \mu_2(\varkappa)=kT\varkappa^2/2m,\quad \mu_{2l+1}(\varkappa)=0.\tag{32}$$

By considering the moments as functions of the real variable κ, we encounter the same problem of their behavior as $\kappa \to 0$. Using the explicit expression for the moment $\mu_4(\kappa)$ and the known capacity of obtaining higher moments,[10] it is easy to derive the result that they will all have as $\kappa \to 0$ principal singularities of the form

$$\mu_{2l}(\varkappa)\sim\varkappa^{4+2l}\ln\varkappa,\quad l\neq1.\tag{33}$$

This suggests that not only the static structure factor but also the more important dynamic form factor of a simple liquid is nonanalytic in $\kappa \to 0$.

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[1] J. Enderby, T. Gaskell, and H. March, Proc. Phys. Soc. (London) **85**, 217 (1965).

[2] H. B. Casimir and D. Polder, Phys. Rev. **73**, 360 (1948).

[3] F. M. Kuni, Dokl. Akad. Nauk SSSR **179**, 129 (1968).

[4] I. Z. Fisher, Statisticheskaya teoriya zhidkosteĭ (Statistical Theory of Liquids) (Fizmatgiz, 1961).

[5] E. M. Lifshitz, Zh. Eksp. Teor. Fiz. **29**, 94 (1955) [Sov. Phys.-JETP **2**, 73 (1956)].

[6] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media) (Fizmatgiz, 1957).

[7] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, Metody kvantovoĭ teorii polya v statisticheskoĭ fizike (Methods of Quantum Field Theory in Statistical Physics) (Fizmatgiz, 1962).

[8] I. S. Gradshteĭn and I. M. Ryzhik, Tablitsy integralov, summ, ryadov i proizvedeniĭ (Tables of Integrals, Sums, Series, and Products) (Fizmatgiz, 1963).

[9] J. Barker, D. Henderson, and W. Smith, Molec. Phys. **17**, 579 (1969).

[10] P. G. deGennes, Physica **25**, 825 (1959).

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