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Abstract

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PHYSICS

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ON A REFINEMENT OF THE SUPERPOSITION APPROXIMATION IN THE THEORY OF LIQUIDS

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The most effective way of applying the general laws of statistical physics to classical condensed systems consists in introducing the apparatus of correlation functions $F_s(q_1, \dots, q_s)$ for groups of s particles ($s = 1, 2, \dots$) and in studying the system of integro-differential equations for them (1):

$$kT\vec{\nabla}_1 F_s + F_s \vec{\nabla} U_s + \frac{1}{v}\int \vec{\nabla}_1 \Phi_{1,s+1} \cdot F_{s+1}\, dq_{s+1} = 0. \tag{1}$$

Here $\Phi_{1,s+1}$ is the mutual potential of the 1st and $(s+1)$-st particles; U_s is the sum of the mutual potentials of the selected group of s particles; $\vec{\nabla}_1$ is the gradient with respect to the coordinates of the 1st particle; v is the mean volume per particle in the system; kT is the product of Boltzmann' s constant and the absolute temperature. In addition, the functions F_s must satisfy the conditions of symmetry, normalization, and weakening of correlations as the particles of the selected group recede from one another (1).

In the case of a liquid, the infinite system of equations (1) does not allow the isolation of a small parameter, and its investigation is greatly hindered. In most work carried out so far, Kirkwood' s "superposition approximation" (1) is used, which truncates the chain of equations (1) at the equation for F_2. In the simplest liquid, by virtue of its homogeneity and isotropy,

$$F_1(q) = 1, \qquad F_2(q, q') = g(|q - q'|), \tag{2}$$

and then the superposition approximation takes the form

$$F_3(q, q', q'') = g(|q - q'|)g(|q - q''|)g(|q' - q''|). \tag{3}$$

Substitution into (1) then leads to a closed integral equation for the function $g(r)$ (1), which has been studied in many works. At present it is known that the superposition approximation qualitatively correctly describes the structure and thermodynamic properties of simple liquids; however, the quantitative results obtained with its aid are insufficiently accurate (2, 3). The entropy, energy, and pressure of the liquid turn out to be noticeably underestimated. In the gas region the superposition approximation leads to correct values of the second and third virial coefficients, but distorts the fourth and higher virial coefficients (1, 4).

In work (5) an attempt was made to go beyond the superposition approximation by introducing into approximation (4) an additional factor:

$$F_3(q, q', q'') = g(|q - q'|)g(|q - q''|)g(|q' - q''|)(1 - \gamma). \tag{4}$$

However, the method used in that work led to the value $\gamma = \text{const}$. This is in obvious contradiction with the normalization and correlation-weakening conditions for F_3, which are satisfied in (3) but not in (4).

Below we propose a new variant of correcting the superposition approximation, close in form to (4), but we shall regard the correction factor as a function of the coordinates of the three particles under consideration and obtain an equation for determining this function. The normalization and correlation-weakening conditions for all functions F_s that occur will then be satisfied automatically.

For this purpose, let us introduce a new "supersuperposition" approximation

$$F_4(q, q', q'', q''') = \frac{F_3(q, q', q'')F_3(q, q', q''')F_3(q, q'', q''')F_3(q', q'', q''')}{F_2(q, q')F_2(q, q'')F_2(q, q''')F_2(q', q'')F_2(q', q''')F_2(q'', q''')}, \tag{5}$$

which truncates the infinite chain of equations (1) one link later than in the case of (3). Here it has been taken into account that $F_1(q) = 1$.

Introduce a new function $\Psi(q, q', q'')$ according to the equation

$$F_3(q, q', q'') = g(|q - q'|)g(|q - q''|)g(|q' - q''|)\Psi(q, q', q''). \tag{6}$$

Taking (2) into account, we then obtain, instead of (5),

$$\begin{aligned} F_4(q, q', q'', q''') = {} & g(|q - q'|)g(|q - q''|)g(|q - q'''|)\times \\ & \times g(|q' - q''|)g(|q' - q'''|)g(|q'' - q'''|)\times \\ & \times \Psi(q, q', q'')\Psi(q, q', q''')\Psi(q, q'', q''')\Psi(q', q'', q'''). \end{aligned} \tag{7}$$

If we require that

$$g(r) \to 1 \quad \text{as } r \to \infty, \tag{8}$$

$$\Psi(q, q', q'') \to 1, \tag{9}$$

when at least one of the three particles recedes to infinity, then the normalization and correlation-weakening conditions for F_3 and F_4, according to (6) and (7), will be satisfied.

Substituting (6) and (7) into the basic equations (1) for $s = 2$ and $s = 3$, we obtain a closed system of equations for the functions g and Ψ. After certain simplifications this system takes the form

$$kT\vec{\nabla}_q \ln g(|q-q'|) + \vec{\nabla}_q \Phi(|q-q'|) +$$

$$+\frac{1}{v}\int \vec{\nabla}_q \Phi(|q-q''|) g(|q-q''|) g(|q'-q''|) \Psi(q,q',q'')\, dq'' = 0; \tag{10}$$

$$kT\vec{\nabla}_q \ln \Psi(q,q',q'') + \frac{1}{v}\int \vec{\nabla}_q \Phi(|q-q'''|) g(|q-q'''|) \times$$

$$\times \{g(|q'-q'''|) g(|q''-q'''|) \Psi(q,q',q''') \Psi(q',q'',q''') \Psi(q,q'',q''') -$$

$$-g(|q'-q'''|)\Psi(q,q',q'') - g(|q''-q'''|)\Psi(q,q'',q'')\}\, dq''' = 0. \tag{11}$$

In this case the conditions (8) and (9) must be satisfied.

From the meaning of the derivation of these equations, one should expect that their solutions will lead to more accurate results than the theory of the superposition approximation. That this is indeed so can be verified from an investigation of the gas case. We shall seek solutions of equations (10) and (11) in the form of series in powers of the density:

$$g(r) = g^{(0)}(r) + \frac{1}{v} g^{(1)}(r) + \frac{1}{v^2} g^{(2)}(r) + \ldots; \tag{12}$$

$$\Psi = \Psi^{(0)} + \frac{1}{v}\Psi^{(1)} + \ldots \tag{13}$$

Applying the usual procedure (^{1}), it is not difficult to find successively $g^{(0)}$, $\Psi^{(0)}$, $g^{(1)}$, etc. It is then easy to verify that, for the function $g^{(r)}$, the solution written out up to and including terms of order $1/v^2$ coincides exactly with the known solution of the original general equations (1), if these too are represented in the form of series in powers of $1/v$ (^{1}). Because of the cumbersome nature of these solutions, we do not write them out here. At the same time it is known that, in the superposition approximation, the exact solution is obtained only up to and including the term of order $1/v$. Moreover, one should expect that the degree of distortion of the subsequent terms of the expansion (12), as compared with the exact solution of equations (1), will be smaller than in the superposition approximation.

The first terms of the expansion (13) for the function Ψ have the form

$$\Psi(q,q',q'') = 1 + \frac{1}{v}\int \left(\exp\left[-\frac{\Phi(|q-q'''|)}{kT}\right]-1\right)\left(\exp\left[-\frac{\Phi(|q'-q'''|)}{kT}\right]-1\right)\times \\ \times\left(\exp\left[-\frac{\Phi(|q''-q'''|)}{kT}\right]-1\right)dq''' + \cdots \tag{14}$$

If one is interested in the pressure of a gas, the result obtained will lead to the fact that in our theory we obtain the exact values of the second, third, and fourth virial coefficients. If it is taken into account that the inclusion of the fifth virial coefficient is essential only for a comparatively very dense gas, then we see that, in the gas case, the theory set forth has sufficient accuracy over a wide range of densities and pressures and surpasses the superposition approximation in accuracy.

It would therefore be of interest to investigate equations (10) and (11) in the case of a liquid. One may hope that this would lead to a more perfect theory than the theory developed up to now, which is based on the superposition approximation. Equations (10) and (11) are complicated; however, the equations proposed with the same aim of correcting the superposition approximation by Kirkwood (^{6}) and Mayer (^{7}) lead to still more complicated and cumbersome equations.

The investigation of equations (10) and (11) will require the use of the resources of machine mathematics, analogous to the study of the superposition approximation in work (^{2}).

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Note: Figure translations are in progress. See original paper for figures.