LONG-RANGE FOUR-PARTICLE CORRELATIONS AT THE CRITICAL POINT

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An investigation is made of the four-particle correlation function which describes the behavior of a simple liquid with a central pair interaction near its critical point and which refers to a configuration of particles when two pairs of closely located particles are separated from each other by a large distance. The explicit form is determined of the terms responsible for contributions to this function which fall off slowly at large distances, the behavior of the specific heat is analyzed and the results are compared with the theory of critical indices.

1. INTRODUCTION

In the paper of one of the authors[1] exact estimates were obtained for all the contributions which fall off slowly with distance to the three-particle distribution function for a classical liquid near its critical point expressed in terms of the two-particle distribution function. In the present paper the same problem is posed for the more interesting four-particle distribution function. As in[1], we consider the equilibrium classical system with the Hamiltonian function:

$$H=\sum_j \mathbf{p}_j^2/2m+\sum_{j<l}\sum \Phi(|\mathbf{r}_i-\mathbf{r}_j|), \tag{1}$$

where $\Phi(r)$ falls off rapidly with increasing r, and we assume as known the two-particle distribution function for an unbounded system $F_2(\mathbf{r}_1, \mathbf{r}_2) = g(|\mathbf{r}_1 - \mathbf{r}_2|)$ normalized by the condition $g(\infty) = 1$. At the same time $F_1(\mathbf{r}_1) = 1$. We shall often refer to the known expressions for the pressure, the average energy density and the isothermal compressibility in such a system[2]:

$$p=nkT-\frac{n^2}{6}\int r\Phi'(r)g(r)d\mathbf{r}, \tag{2}$$

$$\varepsilon=\frac{3}{2}nkT+\frac{n^2}{2}\int\Phi(r)g(r)d\mathbf{r}, \tag{3}$$

$$kT\left(\frac{\partial n}{\partial p}\right)_T=1+n\int(g(r)-1)d\mathbf{r}, \tag{4}$$

where all the notation is standard, and to the expressions for the derivatives with respect to density

$$n\left(\frac{\partial p}{\partial n}\right)_T=2p-nkT-\frac{n^3}{6}\int r\Phi'(r)\frac{\partial g(r)}{\partial n}d\mathbf{r}, \tag{5}$$

$$n\left(\frac{\partial \varepsilon}{\partial n}\right)_T=2\varepsilon-\frac{3}{2}nkT+\frac{n^3}{2}\int\Phi(r)\frac{\partial g(r)}{\partial n}d\mathbf{r}, \tag{6}$$

and also

$$n^2\left(\frac{\partial^2 p}{\partial n^2}\right)_T=4n\left(\frac{\partial p}{\partial n}\right)_T-6p+2nkT-\frac{n^4}{6}\int r\Phi'(r)\frac{\partial^2 g(r)}{\partial n^2}d\mathbf{r}, \tag{7}$$

$$n^2\left(\frac{\partial^2 \varepsilon}{\partial n^2}\right)_T=4n\left(\frac{\partial \varepsilon}{\partial n}\right)_T-6\varepsilon+3nkT+\frac{n^4}{2}\int\Phi(r)\frac{\partial^2 g(r)}{\partial n^2}d\mathbf{r}. \tag{8}$$

At the critical point the integral in (4) diverges, the expressions (5) and (7) vanish, and the expressions (6) and (8) remain finite. In connection with this we assume everywhere in the following that $g(r)$, $\partial g(r)/\partial n$ and $\partial^2 g(r)/\partial n^2$ regarded as functions of r are continuous at small distances and integrable in all the states of the system including the critical point.

Below we shall also require the estimates obtained in[1] for the three-particle distribution function near the critical point. With F_3 represented in the form

$$F_3(\mathbf{r},\mathbf{R})=g(r)+\sum_l A_l(r,R)P_l(\cos\vartheta), \tag{9}$$

where $r = |\mathbf{r}_2 - \mathbf{r}_1|$, $R = |\mathbf{r}_3 - \mathbf{r}_1|$, ϑ is the angle between $(-\mathbf{r})$ and $\mathbf{R}$, for the case $R \gg r$ we have obtained

$$A_0(r,R)=\omega(r)(g(R)-1)+Q_0(r,R), \tag{10}$$

$$\omega(r)=2g(r)+n\partial g(r)/\partial n, \tag{11}$$

$$\int Q_0(r,R)d\mathbf{R}=\partial g(r)/\partial n \tag{12}$$

and further

$$A_1(r,R)={}^1\!/_2 r\omega(r)g'(R)+3Q_1(r,R), \tag{13}$$

$$A_2(r,R)={}^1\!/_8 r^2\omega(r)(g''(R)-g'(R)/R)+5Q_2(r,R), \tag{14}$$

$$A_l(r,R)=(2l+1)Q_l(r,R),\quad l\geqslant 3. \tag{15}$$

It was shown that all the functions $Q_l(r, R)$ fall off with increasing R faster than R^{-3}.

In the present paper we restrict ourselves to the investigation of the most interesting configuration of four particles when the latter constitute two pairs far removed from each other. The distance between the particles in each pair is of the order of the range of the intermolecular interaction, while the distance between pairs is great, but smaller than the correlation radius of critical fluctuations. We use the notation $\mathbf{r}_1 - \mathbf{r}_2 = \mathbf{r}$, $\mathbf{r}_4 - \mathbf{r}_3 = \boldsymbol{\rho}$, $\mathbf{r}_3 - \mathbf{r}_2 = \mathbf{R}$ and we assume that $R \gg r, \rho$. As $R \to \infty$ the function $F_4(\mathbf{r}, \boldsymbol{\rho}, \mathbf{R})$ tends to $g(r)g(\rho)$. Our problem is to determine the asymptotic behavior of the correlation function

$$F_4(\mathbf{r},\boldsymbol{\rho},\mathbf{R})-g(r)g(\rho) \tag{16}$$

as $R \to \infty$ in the immediate neighborhood of the critical point of the system.

The function $F_4(\mathbf{r}, \boldsymbol{\rho}, \mathbf{R})$ must be invariant with respect to all possible rotations and reflections of the system of the four points and with respect to permutations of pairs of particles compatible with the conditions $r, \rho \ll R$. Therefore it depends on six scalar arguments which define the relative position of the four points in space and satisfies additional symmetry conditions. We choose as independent arguments the lengths r, ρ, R, the angles ϑ, ϑ' between the vectors $(-\mathbf{r})$, $\mathbf{R}$ and correspondingly $\boldsymbol{\rho}$, $\mathbf{R}$ and the difference φ of the azimuthal angles of the vector $\mathbf{r}$ and $\boldsymbol{\rho}$ measured with respect to the axis $\mathbf{R}$. The symmetry with respect to reflection in planes containing $\mathbf{R}$ leads to the even dependence of F_4 on φ, and a general expression for the correlation function (16) will turn out to be the double series in spherical harmonics of the form

$$F_4(\mathbf{r},\rho,\mathbf{R})-g(r)g(\rho)=\sum_{l,l'}\sum_m B_{ll'}^m(r,\rho,R)P_l^m(\cos\vartheta)P_{l'}^m(\cos\vartheta')\cos m\varphi. \tag{17}$$

It is obvious that $B_{ll'}^m(r,\rho,R)=B_{l'l}^m(\rho,r,R)$, and for $l'=l$ the functions $B_{ll'}^m(r,\rho,R)$ are symmetric with respect to r and ρ. As a result of the symmetry conditions the functions $B_{ll'}^m(r,\rho,R)$ are not independent of one another.

Our problem reduces to the determination of the asymptotic properties of the functions $B_{ll'}^m(r,\rho,R)$ as $R\to\infty$ near the critical point of the system and to specifying all the relationships significant for $R\gg r$ between the functions $B_{ll'}^m$. It will be shown that this problem is to a significant extent soluble, and the long-range contributions to the correlation of the fluctuations of different physical quantities will be determined.

2. THE ASYMPTOTIC BEHAVIOR OF THE FUNCTION $B_{00}^0(r,\rho,R)$

Of the greatest interest is the function B_{00}^0 with which we begin our analysis. Let $\epsilon(\mathbf{x})$ be the true energy density at the point $\mathbf{x}$ which corresponds to the Hamiltonian function (1)

$$\varepsilon(\mathbf{x})=\sum_j\left\{\frac{\mathbf{p}_j^2}{2m}+\frac{1}{2}\sum_{i\neq j}\Phi(|\mathbf{r}_i-\mathbf{r}_j|)\right\}\delta(\mathbf{x}-\mathbf{r}_j), \tag{18}$$

and let $\Delta\epsilon(\mathbf{x})=\epsilon(\mathbf{x})-\epsilon$, where ϵ is defined by (3). From (18) and from the definition of the distribution function F_S follows the general expression for the correlations of the fluctuations of the energy density at two points of the system:

$$\begin{aligned}\langle\Delta\varepsilon(\mathbf{x})\Delta\varepsilon(\mathbf{x}+\mathbf{R})\rangle=&\left\{\frac{15}{4}n(kT)^2+\frac{3}{2}n^2kT\int\Phi(r)g(r)d\mathbf{r}\right.\\&\left.+\frac{n^2}{4}\int\Phi^2(r)g(r)d\mathbf{r}+\frac{n^3}{4}\iint\Phi(r)\Phi(\rho)F_3(\mathbf{r},\rho)d\mathbf{r}\,d\rho\right\}\delta(\mathbf{R})\\&+\frac{3}{2}n^2kT\Phi(R)g(R)+\frac{n^2}{4}\Phi^2(R)g(R)+\frac{n^3}{4}\int\Phi(r)\Phi(|\mathbf{R}-\mathbf{r}|)F_3(\mathbf{r},\mathbf{R}-\mathbf{r})d\mathbf{r}\\&+\frac{n^3}{2}\Phi(R)\int\Phi(r)F_3(\mathbf{r},\mathbf{R})d\mathbf{r}+\frac{3}{2}n^3kT\int\Phi(r)[F_3(\mathbf{r},\mathbf{R})-g(r)]d\mathbf{r}\\&+\frac{9}{4}(nkT)^2(g(R)-1)+\frac{n^4}{4}\iint\Phi(r)\Phi(\rho)[F_4(\mathbf{r},\rho,\mathbf{R})-g(r)g(\rho)]d\mathbf{r}\,d\rho.\end{aligned} \tag{19}$$

In this expression only the last three terms are sensitive to the critical point. We integrate (19) with respect to $\mathbf{x}$ and $\mathbf{R}$ twice within the limits of a certain large volume V within the system and we divide the result by V. All the terms except for the last one are integrated and an estimate of their value is made with the aid of expressions (3), (4), (6) and the identity[1,3]:

$$2g(r)+n\int[F_3(\mathbf{r},\mathbf{R})-g(r)]d\mathbf{R}=kT\left(\frac{\partial n}{\partial p}\right)_T\omega(r) \tag{20}$$

with $\omega(r)$ from (11). The last term in (19) after integration over $\mathbf{R}$ taking (17) into account leads to the corresponding triple integral in which the expression in square brackets is replaced by $B_{00}^0(r,\rho,R)$. We introduce in place of B_{00}^0 a new unknown function W by means of the relation

$$B_{00}^0(r,\rho,R)=\omega(r)\omega(\rho)(g(R)-1)+W(r,\rho,R). \tag{21}$$

The substitution of this expression into the remaining integral after computing the contributions of the first term in (21) and after summing all the contributions from the right hand side of (19) leads an exact estimate of the quadratic fluctuations of the energy in the volume V in the form

$$\begin{aligned}\frac{1}{V}\langle(\Delta E)^2\rangle=&\frac{3}{2}n(kT)^2-n\left[\left(\frac{\partial\varepsilon}{\partial n}\right)_T-\frac{3}{2}kT\right]^2+nkT\left(\frac{\partial\varepsilon}{\partial n}\right)_T^2\left(\frac{\partial n}{\partial p}\right)_T\\&+\frac{n^2}{2}\int\Phi^2(r)g(r)d\mathbf{r}+n^3\iint\Phi(r)\Phi(\rho)F_3(\mathbf{r},\rho)d\mathbf{r}\,d\rho\\&+\frac{n^4}{4}\iiint\Phi(r)\Phi(\rho)W(r,\rho,R)d\mathbf{r}\,d\rho\,d\mathbf{R}.\end{aligned} \tag{22}$$

The expression obtained above should be compared with the general result for a grand canonical ensemble:

$$\frac{1}{V}\langle(\Delta E)^2\rangle=nkT^2c_V+nkT\left(\frac{\partial\varepsilon}{\partial n}\right)_T^2\left(\frac{\partial n}{\partial p}\right)_T, \tag{23}$$

where c_V is the specific heat for constant N and V evaluated per particle. Comparing (22) and (23) we find that

$$\begin{aligned}c_V=&\frac{3}{2}k-k\left[\frac{1}{kT}\left(\frac{\partial\varepsilon}{\partial n}\right)_T-\frac{3}{2}\right]^2+\frac{n^2}{kT^2}\iint\Phi(r)\Phi(\rho)F_3(\mathbf{r},\rho)d\mathbf{r}\,d\rho\\&+\frac{n}{2kT^2}\int\Phi^2(r)g(r)d\mathbf{r}+\frac{n^3}{4kT^2}\iiint\Phi(r)\Phi(\rho)W(r,\rho,R)d\mathbf{r}\,d\rho\,d\mathbf{R}.\end{aligned} \tag{24}$$

We note that the substitution of (21) guaranteed the exact cancellation in c_V of terms proportional to the isothermal compressibility.

On the right hand side of (24) all the terms except for the last one are insensitive to the critical point. Therefore, the unbounded increase in the specific heat c_V as the critical point is approached, which is known both experimentally and from the solution of model problems, can be associated, according to (24), only with the divergence of the integrals of W over $\mathbf{R}$ at large distances. Therefore we separate out from $W(r,\rho,R)$ the part which asymptotically falls off slowly with increasing R by setting

$$W(r,\rho,R)=\chi(r)\chi(\rho)h(R)+Q_{00}(r,\rho,R), \tag{25}$$

where in the first term the required symmetry with respect to r and ρ has been taken into account. Here $\chi(\rho)$ and $h(R)$ are certain functions which are as yet unknown. Near the critical point $h(R)$ must fall off slowly with increasing R, and with respect to Q_{00}^0 we assume that

$$\left|n\int Q_{00}^0(r,\rho,R)d\mathbf{R}\right|<+\infty. \tag{26}$$

Substituting (25) into (24) we obtain for the specific heat

$$\begin{aligned}c_V=&\frac{3}{2}k-k\left[\frac{1}{kT}\left(\frac{\partial\varepsilon}{\partial n}\right)_T-\frac{3}{2}\right]^2+\frac{n}{2kT^2}\int\Phi^2(r)g(r)d\mathbf{r}\\&+\frac{n^2}{kT^2}\iint\Phi(r)\Phi(\rho)F_3(\mathbf{r},\rho)d\mathbf{r}\,d\rho+\frac{n^3}{4kT^2}\iiint\Phi(r)\Phi(\rho)Q_{00}^0(r,\rho,R)d\mathbf{r}\,d\rho\,d\mathbf{R}\end{aligned}$$

$$+ k\left[\frac{n}{2kT}\int \Phi(r)\chi(r)d\mathbf{r}\right]^2 n\int h(R)d\mathbf{R}.$$

If (26) holds, then the divergence of the integral over $\mathbf{R}$ in the last term of (27) is the only possible cause for the anomaly of the specific heat c_V at the critical point.

We do not have the means for a strictly analytic proof of relation (26) in contrast, for example, to the rigorous proof in[1] of relation (12) in the corresponding three-particle problem. The assumption that $W(r, \rho, R)$ has only one contribution falling off slowly as $R \to \infty$ in accordance with (25) and (26) is apparently justified by all the consequences from it which will be obtained below.

Thus, the function $B^0_{00}(r, \rho, R)$ in accordance with (21) and (25) has near the critical point two different contributions falling off slowly as $R \to \infty$

$$B_{00}{}^0(r,\rho,R) = \omega(r)\omega(\rho)(g(R)-1) + \chi(r)\chi(\rho)h(R) + Q_{00}{}^0(r,\rho,R). \tag{28}$$

These same functions $g(R) - 1$ and $h(R)$ define in accordance with (19) and the estimates following it all further contributions to the correlation function energy density-energy density:

$$\langle\Delta\varepsilon(\mathbf{x})\Delta\varepsilon(\mathbf{x}+\mathbf{R})\rangle \sim \left(n\frac{\partial\varepsilon}{\partial n}\right)_T^2 (g(R)-1) - \left(\frac{n^2}{2}\int\Phi(r)\chi(r)dr\right)^2 h(R). \tag{29}$$

A comparison of (4) and (27) with the well-known experimental fact that the isothermal compressibility has near the critical point a stronger singularity than the specific heat c_V leads to the conclusion that the function $h(R)$ must fall off with increasing R faster than $g(R) - 1$.

Additional information concerning the function $\chi(r)$ can be obtained in the following manner. Directly from the definition of the distribution function F_S in a grand canonical ensemble follows the identity[3]

$$\frac{n^2}{2}\iint \rho\Phi'(\rho)[F_4(\mathbf{r},\boldsymbol{\rho},\mathbf{R}) - g(r)g(\rho)]d\boldsymbol{\rho}\, d\mathbf{R} = -kTrg'(r)$$
$$+3nkT\int[F_3(\mathbf{r},\mathbf{R}) - g(r)]d\mathbf{R} - 2n\int\rho\Phi'(\rho)F_3(\boldsymbol{\rho},\mathbf{r})d\boldsymbol{\rho} - r\Phi'(r)g(r), \tag{30}$$

which is equivalent to the identity $(\partial g(r)/\partial V)_{T,\mu} = 0$. Substituting into (30) the series (17) and utilizing (20), (28) and the expressions (2), (4) we obtain

$$\frac{n^2}{2}\chi(r)\int\rho\Phi'(\rho)\chi(\rho)d\rho\int h(R)d\mathbf{R} = 3n\left(2kT - \left(\frac{\partial p}{\partial n}\right)_T\right)\frac{\partial g(r)}{\partial n}$$
$$-kTrg'(r) + 6\left(kT - \left(\frac{\partial p}{\partial n}\right)_T\right)g(r) - 2n\int\rho\Phi'(\rho)F_3(\mathbf{r},\boldsymbol{\rho})d\boldsymbol{\rho}$$
$$-r\Phi'(r)g(r) - \frac{n^2}{2}\iint\rho\Phi'(\rho)Q_{00}{}^0(r,\rho,R)d\boldsymbol{\rho}\, d\mathbf{R}. \tag{31}$$

At the critical point of the system all the terms of the right hand side of (31) remain finite under the assumption (26) made above, while the left hand side contains a divergent integral of $h(R)$. It is therefore necessary that at the critical point the following condition be satisfied

$$n\int r\Phi'(r)\chi(r)d\mathbf{r} = 0, \tag{32}$$

which to a certain extent makes more precise the properties of the function $\chi(r)$ from (28). Below we shall see that this condition is sufficient for making almost all the required estimates.

Comparing (32) with (7) and taking into account the fact that at the critical point $(\partial^2 p/\partial n^2)_T = 0$, we see that a possible solution of equation (32) is the function

$$\chi(r) = \frac{\partial^2}{\partial n^2}(n^2 g(r)) = 2g(r) + 4n\frac{\partial g(r)}{\partial n} + n^2\frac{\partial^2 g(r)}{\partial n^2}, \tag{33}$$

or, what is the same thing,

$$\chi(r) = \omega(r) + n\,\partial\omega(r)/\partial n. \tag{34}$$

This is the only solution of (32) which depends only on $g(r)$ and which is linear with respect to $g(r)$ and its derivatives with respect to the density. In this case for further contributions to the correlations of the fluctuations of the energy density and the anomalous part of the specific heat we obtain from (29) and (27) with the aid of (8)

$$\langle\Delta\varepsilon(\mathbf{x})\Delta\varepsilon(\mathbf{x}+\mathbf{R})\rangle \sim \left(n\frac{\partial\varepsilon}{\partial n}\right)_T^2 (g(R)-1) + \left(n^2\frac{\partial^2\varepsilon}{\partial n^2}\right)_T^2 h(R), \tag{35}$$

$$c_V \sim k\left(\frac{n}{kT}\left(\frac{\partial^2\varepsilon}{\partial n^2}\right)_T\right)^2 n\int h(R)d\mathbf{R}. \tag{36}$$

Unfortunately we can not prove the necessity of the choice of this particular solution of equation (32) although it appears to be quite plausible.

3. RELATION TO THE DERIVATIVES WITH RESPECT TO TEMPERATURE

The four-particle distribution function $F_4(\mathbf{r}, \boldsymbol{\rho}, \mathbf{R})$ is closely related to the derivative with respect to the temperature of the two-particle distribution function $g(r)$. Directly from the definition of the functions F_S in a grand canonical ensemble the general expression follows:

$$kT^2\frac{\partial g(r)}{\partial T} = g(r)\Phi(r) + n\int[\Phi(\rho) + \Phi(|\mathbf{r}-\boldsymbol{\rho}|)]F_3(\mathbf{r},\boldsymbol{\rho})d\boldsymbol{\rho}$$
$$+\frac{n^2}{2}\iint\Phi(\rho)[F_4(\mathbf{r},\boldsymbol{\rho},\mathbf{R}) - g(r)g(\rho)]d\boldsymbol{\rho}$$
$$-\omega(r)\left[n\int\Phi(\rho)g(\rho)d\boldsymbol{\rho} + \frac{n^2}{2}\iint\Phi(\rho)[F_3(\boldsymbol{\rho},\mathbf{R}) - g(\rho)]d\boldsymbol{\rho}\, d\mathbf{R}\right]. \tag{37}$$

On the left hand side we have the derivative at constant density, the last term on the right hand side corresponds to a recalculation from $(\partial g(r)/\partial T)_{\mu,V}$ in a grand canonical ensemble to $(\partial g(r)/\partial T)_n$ in a canonical ensemble[3]. With the aid of expressions (17), (20), (28) and (3), (6) we can significantly simplify (37) and obtain near the critical point

$$kT^2\frac{\partial g(r)}{\partial T} = \Phi(r)g(r) + \left(\frac{3}{2}kT - \left(\frac{\partial\varepsilon}{\partial n}\right)_T\right)\omega(r) + 2n\int\Phi(\rho)F_3(\mathbf{r},\boldsymbol{\rho})d\boldsymbol{\rho}$$
$$+\frac{n^2}{2}\iint\Phi(\rho)Q_{00}{}^0(r,\rho,R)d\boldsymbol{\rho}\, d\mathbf{R} + \chi(r)\left(\frac{n^2}{2}\int\Phi(\rho)\chi(\rho)d\boldsymbol{\rho}\right)\int h(R)d\mathbf{R}. \tag{38}$$

Because of the last term the derivative $(\partial g(r)/\partial T)_n$ increases without limit as the system approaches the critical point.

Thus, the short range two-particle correlations near the critical point are "anomalous" in the sense that the derivative with respect to the temperature $(\partial g(r)/\partial T)_n$ increases without limit, but at the same time the functions $g(r)$, $(\partial g(r)/\partial n)_T$ and $(\partial^2 g(r)/\partial n^2)_T$ remain bounded and continuous. An analogous result for the Ising model was obtained in[4]. Expressions (30) and (38) explain the seeming contradiction between the bounded nature of $(\partial p/\partial T)_n$ and the unbounded nature of $(\partial\epsilon/\partial T)_n$ at the critical point which follows from the result of a direct differentiation of (2) and (3):

$$\left(\frac{\partial p}{\partial T}\right)_n = nk - \frac{n^2}{6}\int r\Phi'(r)\frac{\partial g(r)}{\partial T}d\mathbf{r}, \qquad (39)$$

$$\left(\frac{\partial \varepsilon}{\partial T}\right)_n = \frac{3}{2}nk + \frac{n^2}{2}\int \Phi(r)\frac{\partial g(r)}{\partial T}d\mathbf{r}. \qquad (40)$$

As a result of (30) the divergent contribution to $\partial g(r)/\partial T$ according to (38) disappears when the integral in (39) is calculated, but remains in the case of (40).

If we multiply (38) term by term by $\frac{1}{2}n^2\Phi(r)$ and integrate over all $\mathbf{r}$ then after simple manipulations we again obtain the expression (27) for c_V. Multiplication by $-n^2 r\Phi'(r)/6$ and integration over all $\mathbf{r}$ leads to the identity for a canonical ensemble:

$$\varepsilon - n\left(\frac{\partial \varepsilon}{\partial n}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_n - p. \qquad (41)$$

Both results confirm the consistency of our estimates (26), (28) and (32).

In conclusion we carry out a comparative estimate of the functions $g(R) - 1$ and $h(R)$ utilizing considerations of the theory of similarity of critical fluctuations[5]. We set

$$g(R) - 1 \sim R^{-1-a}, \quad h(R) \sim R^{-3+b}, \qquad (42)$$

substitute into (4) and (27) and carry out the integration over R indicated there within the limits of a sphere of radius equal to the critical correlation radius R_c. Setting $R_c \sim \tau^{-\mu}$, $\tau = (T - T_c)/T_c$, we obtain the anomalous contributions to the isothermal compressibility and the specific heat c_V on the critical isochore which are respectively proportional to $\tau^{-(2-a)\mu}$ and $\tau^{-b\mu}$. Equating this to the critical indices in standard notation (α is the critical index for the specific heat, $2 - \alpha - 2\beta$ is the critical index for the compressibility, $\mu = (2 - \alpha)/3$) we obtain

$$1 + a = \frac{6\beta}{2-\alpha}, \quad b = \frac{3\alpha}{2-\alpha}, \quad \frac{3-b}{1+a} = \frac{1-\alpha}{\beta}. \qquad (43)$$

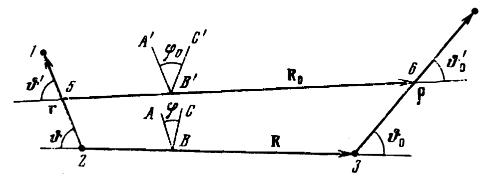
With the estimates $\alpha \approx 0.1$–0.2, $\beta \approx 0.3$–0.4 we obtain $b \approx 0.2$–0.3, $a \approx 0.0$–0.3 and $(3 - b)/(1 + a) \approx 2$. Thus the two long-range terms in (28) differ appreciably in the rate of falling off with increasing R and the function h(R) at large values of R is close to $(g(R) - 1)^2$. The same considerations of the similarity of critical fluctuations together with the estimates given above for $\partial g(r)/\partial T$ lead to the estimate of the temperature dependence of the function g(r) for small values of r on the critical isochor:

$$g(r,\tau) = g_0(r,\tau) + A\tau^{1-\alpha}\chi(r) + \ldots, \qquad (44)$$

where $g_0(r, \tau)$ is a regular function of τ, A is a constant and $\chi(r)$ is the same function as introduced above in (28) with the possible value (34).

4. RELATIONS BETWEEN THE FUNCTIONS $B_{ll'}^m$

In order to determine the asymptotic properties of the leading functions $B_{ll'}^m$ from (17) it is necessary beforehand to establish the relations existing between them due to the symmetry requirements on the function $F_4(\mathbf{r}, \boldsymbol{\rho}, \mathbf{R})$. This can be done rigorously analytically by a method analogous to the one utilized for the same purpose in[1]. Since we are interested only in a small



The relative position of four particles. The segments AB and BC lie on the intersections of the planes 1-2-3, 2-3-4 with the plane perpendicular to the axis R; the segments A'B' and B'C' lie on the intersections of the planes 1-5-6, 5-6-4 with the plane perpendicular to the axis R_0.

number of functions $B_{ll'}^m$ with small indices we can proceed in a simpler and more graphic manner. We introduce in addition to the relative coordinates of the particles $\mathbf{r}, \boldsymbol{\rho}, \mathbf{R}, \vartheta, \vartheta', \varphi$ into (17) the symmetric coordinates $\mathbf{r}, \boldsymbol{\rho}, \mathbf{R}_0, \vartheta_0, \vartheta_0', \varphi_0$, where $\mathbf{R}_0$ is the distance between the midpoints of the segments r and ρ, while the angles $\vartheta_0, \vartheta_0', \varphi_0$ are analogous to the angles $\vartheta, \vartheta', \varphi$, but are measured with reference to $\mathbf{R}_0$ in place of $\mathbf{R}$ (cf., diagram). We have

$$\mathbf{R}_0 = \mathbf{R} + \tfrac{1}{2}(\boldsymbol{\rho} - \mathbf{r}), \quad \mathbf{r}\boldsymbol{\rho} = \text{inv}, \qquad (45)$$

from where one can easily obtain the formulas for the transition from one set of coordinates to the other. It is obvious geometrically that all the symmetry requirements reduce in terms of the new coordinates to the invariance of $F_4(r, \rho, R_0, \vartheta_0, \vartheta_0', \varphi_0)$ with respect to the replacements $\mathbf{r} \to -\mathbf{r}$, $\boldsymbol{\rho} \to -\boldsymbol{\rho}$, carried out separately and together, reflections in planes passing through $\mathbf{R}_0$ and reflections in the plane normal to $\mathbf{R}_0$ and passing through the midpoint of the segment $\mathbf{R}_0$. All these conditions are satisfied by the double series

$$F_4(r,\rho,R_0,\vartheta_0,\vartheta_0',\varphi_0) - g(r)g(\rho) = \sum_{l,l'}\sum_m C_{2l,2l'}^m(r,\rho,R_0)P_{2l}^m(\cos\vartheta_0)P_{2l'}^m(\cos\vartheta_0')\cos m\varphi_0, \qquad (46)$$

which contains in each term only even lower indices and in which $C_{2l,2l'}^m(r, \rho, R_0) = C_{2l',2l}^m(r, \rho, R_0)$. All the coefficients $C_{2l,2l'}^m$ with $l \geq l'$ must be regarded as being independent of one another.

The series (17) is obtained from the series (46) by a term by term transition to the old coordinates, by an expansion in terms of spherical harmonics in terms of the old coordinates and by a regrouping of terms. For $R \gg r, \rho$ all the calculations are carried out in an elementary manner but turn out to be awkward. As a result all the functions $B_{ll'}^m$ turn out to be expressed in terms of the functions $C_{2l,2l'}^m$. Since there are many more functions of the former kind than of the latter kind, then, by eliminating $C_{2l,2l'}^m$, we obtain the complete set of relations between the functions $B_{ll'}^m$. In the course of elimination of $C_{2l,2l'}^m$ it is found automatically that each of these functions in terms of the new arguments can be expressed in terms of the combinations of the functions $B_{ll'}^m$ (and of their derivatives) with only even lower indices, for example:

$$C_{00}^0(r,\rho,R) = B_{00}^0(r,\rho,R) - \frac{r^2+\rho^2}{24}\left(\frac{\partial^2 B_{00}^0}{\partial R^2} + \frac{2}{R}\frac{\partial B_{00}^0}{\partial R}\right)$$
$$C_{02}^0(r,\rho,R) = B_{02}^0(r,\rho,R) - \frac{r^2}{12}\left(\frac{\partial^2 B_{00}^0}{\partial R^2} - \frac{1}{R}\frac{\partial R_{00}^0}{\partial R}\right) + \ldots \qquad (47)$$

etc. On the right hand side in each line we have not shown terms of higher orders of smallness with respect to r/R and ρ/R. Substitution into the remaining equations for the case $R \gg r, \rho$ leads to an explicit expression for all the $B^m_{ll'}$ (with at least one odd lower index) in terms of $B^m_{ll'}$ with two even lower indices, including zero. For example, we have

$$B_{10}^0 = \frac{r}{2}\frac{\partial}{\partial R}\left\{B_{00}^0 - \frac{r^2+\rho^2}{60}\Delta_R B_{00}^0\right\} + \frac{r}{5}\left\{\frac{\partial B_{20}^0}{\partial R} + \frac{3}{R}B_{20}^0\right\}$$
$$B_{11}^0 = \frac{r\rho}{4}\frac{\partial^2 B_{00}^0}{\partial R^2} + \ldots \tag{48}$$

etc. Here Δ_R is the Laplacian operator in the space of R, and terms of higher orders of smallness have again been omitted. More complete formulas in somewhat different form will be given below. Thus, in the series (17) we should regard only the coefficients of the form $B^m_{2l,2l'}$ as independent, while all the remaining ones can be expressed in terms of them.

In connection with the result obtained above concerning the long-range contributions to the function B^0_{00} near the critical point it is useful to separate from the earlier functions $B^m_{ll'}$ terms which are directly connected to the function g(R), h(R) and to their lower order derivatives. From (47) and (48) it can be seen that such contributions from B^0_{00} appear in the case of $B^m_{ll'}$ independently of the parity of the lower indices. Together with B^0_{00} there are in all seven such functions containing g(R), g′(R), g″(R) and h(R), h′(R) or terms of the type g(R)/R etc. which are equivalent to them in order of smallness. Such functions with an explicit indication of the terms separated out are

$$B_{00}^0 = \omega(r)\omega(\rho)(g(R)-1) + \chi(r)\chi(\rho)h(R) + Q_{00}^0,$$
$$B_{10}^0 = {}^1/_2 r\{\omega(r)\omega(\rho)g'(R) + \chi(r)\chi(\rho)h'(R)\} + 3Q_{10}^0,$$
$$B_{01}^0(r,\rho,R) = B_{10}^0(\rho,r,R), \qquad B_{11}^0 = {}^1/_4 r\rho\omega(r)\omega(\rho)g''(R) + 9Q_{11}^0,$$
$$B_{11}^1 = -r\rho\omega(r)\omega(\rho)g'(R)/4R + {}^9/_4 Q_{11}^1,$$
$$B_{20}^0 = {}^1/_{12} r^2\omega(r)\omega(\rho)(g''(R) - g'(R)/R) + 5Q_{20}^0,$$
$$B_{02}^0(r,\rho,R) = B_{20}^0(\rho,r,R). \tag{49}$$

These expressions are analogous to expressions (10), (13), (14) in the three-particle problem. In order to make the notation for all the remaining functions $B^m_{ll'}$ uniform we set

$$B^m_{ll'} = (2l+1)(2l'+1)\frac{(l-m)!(l'-m)!}{(l+m)!(l'+m)!}Q^m_{ll'}, \quad l, l' > 2 \tag{50}$$

and regard all the $Q^m_{ll'}$ as new unknown functions instead of $B^m_{ll'}$. Here we have $Q^m_{ll'}(r, \rho, R) = Q^m_{l'l}(\rho, r, R)$. Substitution of (49), (50) into the complete set of equations of the type (48) leads to an explicit expression for the asymptotic values for $R \to \infty$ of the functions $Q^m_{ll'}$ with odd lower indices in terms of the asymptotic values of the "even" functions $Q^m_{ll'}$. For the lower functions $Q^m_{ll'}$ we obtain in this way the relations required later

$$Q_{10}^0 = \frac{r}{6}\left\{\frac{\partial Q_{00}^0}{\partial R} - \frac{r^2+\rho^2}{60}\omega(r)\omega(\rho)(\Delta_R g(R))' + 2\left(\frac{\partial Q_{20}^0}{\partial R} + \frac{3}{R}Q_{20}^0\right) + \ldots\right\}$$
$$Q_{12}^0 = \frac{r}{6}\left\{\frac{\partial Q_{02}^0}{\partial R} + \frac{1}{2R}Q_{22}^1 + 2\left(\frac{\partial Q_{22}^0}{\partial R} + \frac{3}{R}Q_{22}^0\right) + \ldots\right\},$$
$$Q_{12}^1 = r\left\{-\frac{1}{R}Q_{02}^0 + \frac{2}{5R}Q_{22}^0 + \frac{1}{12}\left(\frac{\partial Q_{22}^1}{\partial R} + \frac{3}{R}Q_{22}^1\right) + \frac{1}{24R}Q_{22}^2 + \ldots\right\} \tag{51}$$

etc. (The expressions for Q^0_{11} and Q^1_{11} are omitted because of their awkward form). One should add to this the expressions analogous to (51) for Q^0_{01}, Q^0_{21}, Q^1_{21} which differ from those written out above by permutations of the lower indices and the letters r and ρ. In (51) in the function Q^0_{10} we have retained as an example the term with the third derivative of g(R). Analogous terms with higher order derivatives of g(R) and h(R) occur in (51) and in all the subsequent functions. Moreover, we have not written out the terms with derivatives of higher orders than indicated of the different "even" functions.

5. ASYMPTOTIC BEHAVIOR OF THE FUNCTIONS $Q^m_{ll'}$

For all the functions $Q^m_{ll'}$ with $l = 1$ or $l' = 1$, m = 0, 1, one can obtain explicit asymptotic estimates for $R \to \infty$ if one utilizes the equation from the chain of Bogolyubov[6] equations relating the distribution functions F_3 and F_4:

$$kT\frac{\partial F_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)}{\partial \mathbf{r}_1} + F_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\frac{\partial U_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)}{\partial \mathbf{r}_1}$$
$$+ n\int\frac{\partial\Phi(|\mathbf{r}_1-\mathbf{r}_4|)}{\partial\mathbf{r}_1}F_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)d\mathbf{r}_4 = 0, \tag{52}$$

where

$$U_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \Phi(|\mathbf{r}_1-\mathbf{r}_2|) + \Phi(|\mathbf{r}_1-\mathbf{r}_3|) + \Phi(|\mathbf{r}_3-\mathbf{r}_2|).$$

In terms of the coordinates r, ρ, R, ϑ, ϑ′, φ the projections of the vector equation (52) along the direction of **R** and on the plane normal to **R** yield

$$n\int\Phi'(\rho)F_4(\mathbf{r},\rho,\mathbf{R})\cos\vartheta'\,d\rho = kT\frac{\partial F_3(\mathbf{r},\mathbf{R})}{\partial R}$$
$$+ F_3(\mathbf{r},\mathbf{R})\left(\Phi'(R) + \frac{\partial}{\partial R}\Phi(|\mathbf{R}-\mathbf{r}|)\right),$$
$$n\int\Phi'(\rho)F_4(\mathbf{r},\rho,\mathbf{R})\sin\vartheta'\cos\varphi\,d\rho = -\frac{\sin\vartheta}{R}$$
$$\times\left\{kT\frac{\partial F_3(\mathbf{r},\mathbf{R})}{\partial(\cos\vartheta)} + F_3(\mathbf{r},\mathbf{R})\frac{\partial\Phi(|\mathbf{R}-\mathbf{r}|)}{\partial(\cos\vartheta)}\right\}. \tag{53}$$

Substituting into this the series (9) and (17) we obtain the equations

$$\sum_l\left\{\frac{n}{3}\int\Phi'(\rho)B_{l1}^0(r,\rho,R)d\rho - kT\frac{\partial A_l(r,R)}{\partial R} - \Phi'(R)(g(r)\delta_{0l}\right.$$
$$\left.+ A_l(r,R))\right\}P_l(\cos\vartheta) = \frac{\partial\Phi(|\mathbf{R}-\mathbf{r}|)}{\partial R}F_3(\mathbf{r},\mathbf{R}),$$
$$\sum_l\left\{\frac{n}{3}\int\Phi'(\rho)B_{l1}^1(r,\rho,R)d\rho + \frac{kT}{R}A_l(r,R)\right\}P_l^1(\cos\vartheta)$$
$$= -\frac{\sin\vartheta}{R}\frac{\partial\Phi(|\mathbf{R}-\mathbf{r}|)}{\partial(\cos\vartheta)}F_3(\mathbf{r},\mathbf{R}). \tag{54}$$

Expansion of the right hand sides in series in terms of $P_l(\cos\vartheta)$ and $P^1_l(\cos\vartheta)$ leads to two infinite systems of equations for B^0_{l1} and B^1_{l1}.

In order to obtain asymptotic estimates for $R \to \infty$ one can neglect in (54) all terms containing the factors Φ(R), Φ(|**R** − **r**|) and their derivatives. We then obtain the simple relations:

$$n\int\Phi'(\rho)B_{l1}^0(r,\rho,R)d\rho = 3kT\frac{\partial A_l(r,R)}{\partial R} + \ldots,$$
$$n\int\Phi'(\rho)B_{l1}^1(r,\rho,R)d\rho = -\frac{3kT}{R}A_l(r,R) + \ldots. \tag{55}$$

For $l = 0$ and $l = 1$ with the aid of (4), (5), (10), (12), (14), (32), (49) we obtain after some manipulations the integral estimates

$$\frac{n^2}{2}\iint\Phi'(\rho)RQ_{01}^0(r,\rho,R)d\rho\,d\mathbf{R}$$

$$= -\frac{3}{2}\left(kT - \left(\frac{\partial p}{\partial n}\right)_T\right)\omega(r) - \frac{3}{2}nkT\frac{\partial g(r)}{\partial n} + \ldots,$$

$$\frac{n^2}{2}\iint \Phi'(\rho)R^2Q_{11}{}^0(r,\rho,R)\,d\rho\,d\mathbf{R}$$

$$= \left(kT - \left(\frac{\partial p}{\partial n}\right)_T\right)r\omega(r) - 2nkT\int RQ_1(r,R)\,d\mathbf{R} + \ldots,$$

$$\frac{n^2}{2}\iint \Phi'(\rho)R^2Q_{11}{}^1(r,\rho,R)\,d\rho\,d\mathbf{R}$$

$$= \left(kT - \left(\frac{\partial p}{\partial n}\right)_T\right)r\omega(r) - \frac{2}{3}nkT\int RQ_1(r,R)\,d\mathbf{R} + \ldots. \quad (56)$$

According to estimates from[1] the function $Q_1(\mathbf{r}, R)$ falls off with increasing R faster than R^{-4}. Therefore the right hand sides of (56) remain finite at the critical point, and we conclude that the pair of functions Q_{01}^0 and Q_{10}^0 falls off with increasing R faster than R^{-4}, while the pair of functions Q_{11}^0 and Q_{11}^1 falls off faster than R^{-5}. For $l = 2$ we obtain in an analogous manner the integral estimates:

$$\frac{n^2}{2}\iint \Phi'(\rho)RQ_{21}{}^0(r,\rho,R)\,d\rho\,d\mathbf{R}$$

$$= -\frac{9}{80}nkTr^2\omega(r)\int\frac{g(R)-1}{R^2}d\mathbf{R} - \frac{3}{2}nkT\int Q_2(r,R)\,d\mathbf{R} + \ldots,$$

$$\frac{n^2}{2}\iint \Phi'(\rho)RQ_{21}{}^1(r,\rho,R)\,d\rho\,d\mathbf{R}$$

$$= -\frac{9}{20}nkTr^2\omega(r)\int\frac{g(R)-1}{R^2}d\mathbf{R} - 6nkT\int Q_2(r,R)\,d\mathbf{R} + \ldots. \quad (57)$$

In accordance with[1] the function $Q_2(\mathbf{r}, R)$ falls off with increasing R faster than R^{-3}. If, moreover, in (42) $a > 0$, then the right hand sides of (57) remain finite at the critical point, and we conclude that the four functions Q_{21}^0, Q_{12}^0, Q_{21}^1 and Q_{12}^1 fall off with increasing R faster than R^{-4}. But if in (42) $a = 0$ and $g(R) - 1 \sim 1/R$, then these functions fall off at the critical point like R^{-4}.

Formulas (31), (32) give an exact integral estimate for Q_{00}^0 from which it follows that at the critical point this function falls off with increasing R faster than R^{-3}. Finally from (50) and (55) for $l > 2$ one can obtain the estimates

$$\frac{n^2}{2}\iint \Phi'(\rho)RQ_{l1}{}^0(r,\rho,R)\,d\rho\,d\mathbf{R} = -\frac{3}{2}nkT\int Q_l(r,R)\,d\mathbf{R} + \ldots, \quad l > 2,$$

$$\frac{n^2}{2}\iint \Phi'(\rho)RQ_{l1}{}^1(r,\rho,R)\,d\rho\,d\mathbf{R} = -l(l+1)nkT\int Q_l(r,R)\,d\mathbf{R} + \ldots, \quad l > 2. \quad (58)$$

In accordance with the estimates for Q_l from[1] it follows from here that at the critical point all the functions Q_{l1}^0, Q_{1l}^0, Q_{l1}^1, Q_{1l}^0 with $l > 2$ fall off with increasing R not slower than R^{-4}.

Although we do not have at our disposal exact integral equations for the next coefficients in the expansion (17) we can obtain some information concerning the functions Q_{20}^0, Q_{02}^0, Q_{22}^0, Q_{22}^1, and Q_{22}^2 from the following considerations. If in expressions (51) and analogous ones for the coefficients Q_{11}^0 and Q_{11}^1 we restrict ourselves to contributions of the second order in r/R and ρ/R we obtain a closed system of five differential equations with respect to the functions indicated above. Since the order of smallness of the right hand side and the left hand side of the equations must coincide, the order of each of these functions must be lower by not more than unity than in the case of Q_{21}^0 and Q_{21}^1 estimates for which are given in (57); in other words, the functions indicated above fall off with increasing R faster than R^{-3}.

6. DISCUSSION OF RESULTS

We have carried out all the possible estimates for the first several coefficients of the series (17) in which we have taken into account distant and moderately distant contributions to the four-point distribution function for a classical liquid near its critical point. It is difficult to obtain estimates for the remaining coefficients. However, if one assumes that in a homogeneous and isotropic liquid there are no dominant angular correlations for two pairs of particles as the separation of the pairs from one another is made infinite, then, apparently, all the essential singularities of the function F_4 at the critical point have been taken into account in this paper.

The estimates obtained in Sec. 5 for the remainders of the functions B_{ll}^m, are directly applicable to the study of the correlators energy density-stress tensor and stress tensor-stress tensor. Considering individually the correlators containing a diagonal part and a deviator of the stress tensor one can easily verify that none of them contain near the critical point contributions falling off slowly with distance.

We note that contributions responsible for the behavior of the function F_4 in the critical region are obtained from exact integral equations and in their form differ appreciably from many approximations frequently utilized for this function, among them Kirkwood's superposition approximation. If in the series (17) we restrict ourselves to the principal terms which do not contain any angular dependence, the function F_4 satisfies the hypothesis of conformal invariance[7] and the hypothesis concerning the "coalescence of correlations" (cf.,[8]).

[1] I. Z. Fisher, Zh. Eksp. Teor. Fiz. **62**, 1548 (1972) [Sov. Phys.-JETP **35**, 811 (1972)].

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

[3] P. Schofield, Proc. Phys. Soc. (London) **88**, 149 (1966).

[4] M. A. Mikulinskiĭ, Zh. Eksp. Teor. Fiz. **58**, 1848 (1970) [Sov. Phys.-JETP **31**, 991 (1970)].

[5] V. L. Pokrovskiĭ, Usp. Fiz. Nauk **94**, 128 (1968) [Sov. Phys.-Uspekhi **11**, 66 (1968)].

[6] N. N. Bogolyubov, Izbr. trudy (Selected works), **2**, Naukova Dumka, 1970.

[7] A. M. Polyakov, ZhETF Pis. Red. **12**, 538 (1970) [JETP Lett. **12**, 381 (1970)].

[8] A. M. Polyakov, Zh. Eksp. Teor. Fiz. **57**, 271 (1969) [Sov. Phys.-JETP **30**, 151 (1970)].

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