Long-Range Three-Particle Correlations at the Critical Point

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The contributions to the three-particle correlation function near the critical point of a system, which decrease slowly with the distance, are estimated for a classical liquid with pair and central interaction. Three-particle configurations in which two particles remain at a small distance from each other and the third is removed to infinity are discussed. All slowly decreasing terms of the three-particle correlation function are determined explicitly and expressed in terms of the pair correlation function and its derivatives. The results are used to analyze fluctuation correlations between the particle density and energy density and fluctuation correlations between the particle density and elastic stresses near the critical point of a simple liquid.

1. INTRODUCTION

THE analysis of critical fluctuation is usually confined to a study of long-range two-particle correlations. Yet considerable interest attaches also to multiparticle long-range correlations near the critical point or second-order phase transition points. Some general results with the framework of scaling invariance and especially for the two-dimensional Ising model were obtained in[1,2]. We are interested in the vicinity of the critical point of a classical liquid. As a realistic model of the latter, we assume a system of point-like particles with central and pair interactions, so that the Hamiltonian is equal to

$$H=\sum_j \frac{\mathbf{p}_j^2}{2m}+\sum_{j<l}\Phi(|\mathbf{R}_j-\mathbf{R}_l|), \tag{1}$$

and the function $\Phi(r)$ decreases rapidly with increasing r. Let $g(|\mathbf{R}_2-\mathbf{R}_1|)$ be the equilibrium two-particle distribution after going over to an unbounded system, and let it be normalized by the condition $g(\infty)=1$. Knowledge of the functions $\Phi(r)$ and $g(r)$ makes it possible, as is well known[3,4], to determine the pressure p, the energy density ϵ, and the isothermal compressibility β_T in the form

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

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

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

where n is the average particle-number density. From this follow also the relations

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

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

which will be frequently used in what follows.

At the critical point, the correlation function $g(r)-1$ becomes slowly decreasing with increasing r, and the integral in (4) diverges. However, at small distances, on the order of the effective radius of the intermolecular forces, the function g(r) is finite and continuous. Similar properties are assumed also for $(\partial g(r)/\partial n)_T$ regarded as a function of r, in accord with Eqs. (5) and (6).

We shall investigate the properties of the three-particle distribution function $F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ near the critical point of the system, for the most interesting configuration of a triad of particles, in which two are close to each other and the third is situated at a distance that is very large but still smaller than the critical correlation radius. As $|\mathbf{R}_3|\to\infty$, we should get $F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)\to g(|\mathbf{R}_2-\mathbf{R}_1|)$. We are interested in the behavior of the correlation function $F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) - g(|\mathbf{R}_2-\mathbf{R}_1|)$ as $|\mathbf{R}_3|\to\infty$ in the possibility of determining, near the critical point, all its slowly-decreasing contributions. We present below a complete solution of this problem, expressed in terms of the long-range contributions to $g(r)-1$. We consider also the ensuing consequences with respect to the correlations of the physical quantities at the critical point.

2. CHOICE OF REPRESENTATION FOR F_3 AND SYMMETRY CONDITIONS

For a homogeneous and isotropic system, the function $F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ depends only on three scalar arguments, which determine the relative positions of the points $\mathbf{R}_1$, $\mathbf{R}_2$, and $\mathbf{R}_3$. We choose these arguments to be the lengths r and R of the vectors $\mathbf{r}=\mathbf{R}_2-\mathbf{R}_1$ and $\mathbf{R}=\mathbf{R}_3-\mathbf{R}_1$, and the external angle ϑ between them, so that $\mathbf{r}\cdot\mathbf{R}=-rR\cos\vartheta$. We assume that $R\gg r$. We then expand the correlation deviation $F_3(r, R, \cos\vartheta)-g(r)$ in a series of Legendre polynomials of $\cos\vartheta$, so that

$$F_3(r,R,\cos\vartheta)=g(r)+\sum_l A_l(r,R)P_l(\cos\vartheta). \tag{7}$$

from the condition for the weakening of the Bogolyubov correlations[4] it follows that

$$A_l(r,R)\to 0 \quad \text{при} \quad R\to\infty \tag{8}$$

for all l and independently of the degree of proximity of the system to the critical point.

Not all the coefficients A_l of the series (7) are independent. Permutation of the points $\mathbf{R}_1$ and $\mathbf{R}_2$ does not change the function $F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$. In our notation this means that the series (7) should be invariant when the arguments R and ϑ are replaced by the arguments $\bar{R}$ and $\bar{\vartheta}$ indicated in the figure:

$$\sum_l A_l(r,R)P_l(\cos\vartheta)=\sum_m A_m(r,\bar{R})P_m(\cos\bar{\vartheta}). \tag{9}$$

The analytic connection between $\bar{R}$, $\bar{\vartheta}$ and R, ϑ, as follows directly from the figure, is

$$\bar{R}=\sqrt{R^2+2rR\cos\vartheta+r^2},\quad \cos\bar{\vartheta}=-\frac{R\cos\vartheta+r}{\sqrt{R^2+2rR\cos\vartheta+r^2}}. \tag{10}$$

Multiplying (9) by some $P_n(\cos\vartheta)$ and integrating with a weight $\sin\vartheta$ with respect to ϑ from 0 to π, we get

$$A_l(r,R)=\frac{2l+1}{2}\sum_m(-1)^m\int_0^\pi A_m(r,\bar R)P_m(|\cos\bar\vartheta|)P_l(\cos\vartheta)\sin\vartheta\,d\vartheta \tag{11}$$

for all l, and in the right-hand side it is necessary to substitute in place of $\bar R$ and $\cos\bar\vartheta$ their values from (10).

It follows from (11) that only half of the complete set of the functions A_l (say, all the A_l with even numbers) are independent, and the remaining ones (say A_l with odd numbers) can be expressed in their terms. We confine ourselves here to a direct calculation of this property only in the first order in r/R. Putting $\cos\vartheta = x$, expansion in powers of the ratio r/R yields

$$A_m(r,\bar R)=A_m(r,\sqrt{R^2+2rR\cos\vartheta+r^2})=A_m(r,R)+rx\frac{\partial A_m(r,R)}{\partial R}+\dots, \tag{12}$$

$$P_m(|\cos\bar\vartheta|)=P_m\left(\frac{Rx+r}{\sqrt{R^2+2rRx+r^2}}\right)=P_m(x)-\frac{r}{R}(x^2-1)P_m'(x)+\dots$$
$$\dots=P_m(x)+\frac{r}{R}\frac{m(m+1)}{2m+1}[P_{m-1}(x)-P_{m+1}(x)]+\dots. \tag{13}$$

Substituting this in (11) and using the simple properties of the Legendre polynomials, we obtain for all $l \geq 1$

$$[1-(-1)^l]A_l(r,R)=(-1)^{l-1}\frac{rl}{2l-1}\left[\frac{\partial A_{l-1}(r,R)}{\partial R}-\frac{l-1}{R}A_{l-1}(r,R)\right]$$
$$+(-1)^{l+1}\frac{r(l+1)}{2l+3}\left[\frac{\partial A_{l+1}(r,R)}{\partial R}+\frac{l+2}{R}A_{l+1}(r,R)\right] \tag{14}$$

This system of equations breaks up into two subsystems with odd and even l, respectively. In the former case we obtain directly, at the accuracy spelled out in (14), an expression for all A_l with odd l in terms of the A_l with even l. When a large number is taken into account in the right-hand side of (14), the same problem is solved with higher accuracy by successive approximations. In the second case, for even l in (14), we obtain a subsystem of equations for A_l as a consequence of the preceding subsystem, as can be readily verified by writing out explicitly the nearest succeeding terms of the expansions (12)–(14).

It follows thus from (14) that

$$A_{2l+1}(r,R)=\frac{r(2l+1)}{2(4l+1)}\left[\frac{\partial A_{2l}(r,R)}{\partial R}-\frac{2l}{R}A_{2l}(r,R)\right]$$
$$+\frac{r(l+1)}{4l+5}\left[\frac{\partial A_{2l+2}(r,R)}{\partial R}+\frac{2l+3}{R}A_{2l+2}(r,R)\right]+\dots. \tag{15}$$

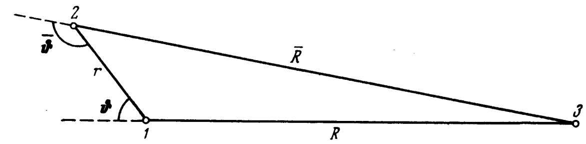
The terms not written out here contain at the very least the third derivatives of the functions $A_l(r, R)$ with even numbers with respect to R, or the terms equivalent to them in order of smallness.

3. LONG-RANGE BEHAVIOR OF THE FUNCTION $A_0(\mathbf{r}, \mathbf{R})$

Our purpose is to separate the slowly-decreasing long-range contributions to the functions $A_l(r, R)$. Greatest interest attaches to the function $A_0(\mathbf{r}, R)$, which we determine from the equation

$$2g(r)+n\frac{\partial g(r)}{\partial n}=\frac{2g(r)-n\int[F_3(r,R,\cos\vartheta)-g(r)]d\mathbf{R}}{1+n\int[g(R)-1]d\mathbf{R}} \tag{16}$$

from Schofield's chain of equations[5] that follow



directly from the grand Gibbs distribution. Substitution of the series (7) in Eq. (16) yields to the following equation for $A_0(\mathbf{r}, \mathbf{R})$:

$$2g(r)+n\frac{\partial g(r)}{\partial n}=\frac{2g(r)+n\int A_0(r,R)d\mathbf{R}}{1+n\int[g(R)-1]d\mathbf{R}}. \tag{17}$$

We introduce in lieu of $A_0(\mathbf{r}, \mathbf{R})$ a new unknown function $Q_0(\mathbf{r}, \mathbf{R})$ defined by

$$A_0(r,R)=\left(2g(r)+n\frac{\partial g(r)}{\partial n}\right)(g(R)-1)+Q_0(r,R). \tag{18}$$

Substituting (18) in (17) we obtain an integral equation for $Q_0(\mathbf{r}, \mathbf{R})$

$$n\int Q_0(r,R)d\mathbf{R}=n\frac{\partial g(r)}{\partial n}. \tag{19}$$

The right-hand side here is finite at the critical point, so that the function $Q_0(\mathbf{r}, \mathbf{R})$ is integrable over all of $\mathbf{R}$ space, and consequently decreases more rapidly than R^{-3} at large R, no matter how close the system is the critical point. Thus, expressions (18) and (19) solve the problem of separating the slowly-decreasing part of the function $A_0(\mathbf{r}, \mathbf{R})$ near the critical point.

As an example of an application of the result, let us consider the spatial correlation of the fluctuations of the particle-number density and of the energy density. For these densities we have

$$n(\mathbf{r})=\sum_j\delta(\mathbf{r}-\mathbf{R}_j), \tag{20}$$

$$\varepsilon(\mathbf{r}')=\sum_j\left\{\frac{\mathbf{p}_j^2}{2m}+\frac{1}{2}\sum_{l\neq j}\Phi(|\mathbf{R}_j-\mathbf{R}_l|)\right\}\delta(\mathbf{r}'-\mathbf{R}_j). \tag{21}$$

Multiplying these expressions by each other, introducing the deviations $\Delta n(\mathbf{r}) = n(\mathbf{r}) - n$, $\Delta\epsilon(\mathbf{r}') = \epsilon(\mathbf{r}') - \epsilon$, and averaging with the aid of the distribution functions $F_1(\mathbf{R}_1) = 1$, $F_2(\mathbf{R}_1, \mathbf{R}_2) = g(|\mathbf{R}_2 - \mathbf{R}_1|)$ and $F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ from (7), we obtain

$$\langle\Delta n(\mathbf{r})\Delta\varepsilon(\mathbf{r}')\rangle=\varepsilon\delta(\mathbf{r}-\mathbf{r}')+\frac{n^2}{2}\Phi(|\mathbf{r}-\mathbf{r}'|)g(|\mathbf{r}-\mathbf{r}'|)$$
$$+\frac{n^3}{2}\int\Phi(\rho)Q_0(\rho,|\mathbf{r}-\mathbf{r}'|)d\rho+n^2\left(\frac{\partial\varepsilon}{\partial n}\right)_T(g(|\mathbf{r}-\mathbf{r}'|)-1), \tag{22}$$

where we used (3), (6), and (18). The last term here is sensitive to the critical point, and at large $|\mathbf{r} - \mathbf{r}'|$ we obtain the long-range correlations of the particle-number-density and energy-density fluctuations in the form

$$\langle\Delta n(0)\Delta\varepsilon(\mathbf{R})\rangle\approx n^2\left(\frac{\partial\varepsilon}{\partial n}\right)_T(g(R)-1). \tag{23}$$

Double integration of (22) with respect to $\mathbf{r}$ and $\mathbf{r}'$ over some large volume leads, after certain transformations, to an exact relation for a grand ensemble

$$\langle\Delta N\Delta E\rangle=\left(\frac{\partial E}{\partial N}\right)_{T,V}\langle(\Delta N)^2\rangle. \tag{24}$$

4. LONG-RANGE BEHAVIOR OF THE FUNCTION $A_1(\mathbf{r}, \mathbf{R})$

We proceed now to estimate the behavior, at large distances, of the function $A_1(\mathbf{r}, \mathbf{R})$. We use for this purpose an equation from the chain of Bogolyubov equations. This equation connects the distribution functions F_2 and F_3. In our notation, this equation is written in the form

$$kTg'(R)+\Phi'(R)g(R)=n\int\Phi'(r)\cos\vartheta F_3(r,R,\cos\vartheta)\,d\mathbf{r}. \quad (25)$$

Substituting here the series (7), we obtain

$$kTg'(R)+\Phi'(R)g(R)=\frac{n}{3}\int\Phi'(r)A_1(r,R)\,d\mathbf{r}. \quad (26)$$

We introduce in place of $A_1(r, R)$ a new unknown function $Q_1(r, R)$ defined by the relation

$$A_1(r,R)=\frac{r}{2}\left(2g(r)+n\frac{\partial g(r)}{\partial n}\right)g'(R)+3Q_1(r,R). \quad (27)$$

Then substituting in (26) with (2) and (5) taken into account leads to an equation for Q_1 in the form

$$n\int\Phi'(r)Q_1(r,R)\,d\mathbf{r}=\left(\frac{\partial p}{\partial n}\right)_T g'(R)+\Phi'(R)g(R). \quad (28)$$

We put temporarily

$$Q_1(r,R)=r\frac{\partial\tilde{Q}_1(r,R)}{\partial R},\quad \tilde{Q}_1(r,\infty)=0. \quad (29)$$

Integrating (28) with respect to R from ∞ to R and multiplying the entire line by n, we obtain

$$n^2\int r\Phi'(r)\tilde{Q}_1(r,R)\,d\mathbf{r}=n\left(\frac{\partial p}{\partial n}\right)_T(g(R)-1)+n\int_\infty^R\Phi'(r)g(r)\,dr. \quad (30)$$

We integrate the resultant equation term by term over all of **R** space. After integrating the last term by parts and using relations (2), (4), and (5), we obtain

$$n\int r\Phi'(r)\left\{n\int\tilde{Q}_1(r,R)\,dR-\frac{n}{6}\left(\frac{\partial g(r)}{\partial n}\right)\right\}d\mathbf{r}=0. \quad (31)$$

If we put

$$n\int\tilde{Q}_1(r,R)\,d\mathbf{R}=\frac{n}{6}\frac{\partial g(r)}{\partial n}+\psi(r), \quad (32)$$

where $\psi(r)$ is a certain function satisfying the condition

$$n\int r\Phi'(r)\psi(r)\,d\mathbf{r}=0, \quad (33)$$

then Eq. (31) is satisfied identically.

We note now that Eqs. (31)–(33) are insensitive to the proximity to the critical point, and remain the same after going to the limit at this point itself. Thus the function $\tilde{Q}_1(r, R)$ is integrable over all of **R** space in all states of the system, and for the function $Q_1(r, R)$ we obtain in accord with (29) a stronger condition in the form

$$\left|n\int RQ_1(r,R)\,d\mathbf{R}\right|<\infty. \quad (34)$$

Expressions (27) and (34) solve completely the problem of separating that part of the function of $A_1(r, R)$ which decreases as $R\to\infty$, near the critical point.

5. LONG-RANGE BEHAVIOR OF THE FUNCTION $A_2(r, R)$

To estimate the behavior of the function $A_2(r, R)$ near the critical point, we no longer have exact integral equations of the type (16) or (25). Some conclusion can be drawn, however, on the basis of relations (14) at $l = 0$. Taking into account the highest-order term of the expansion of $A_0(r, R)$, which has not been written out in (14), we have

$$A_1(r,R)=\frac{\partial}{\partial R}\left\{\frac{r}{2}A_0(r,R)-\frac{r^2}{40}\Delta_R A_0(r,R)\right\}$$
$$+\frac{r}{5}\left\{\frac{\partial A_2(r,R)}{\partial R}+\frac{3}{R}A_2(r,R)\right\}+\ldots, \quad (35)$$

where Δ_R is the Laplace operator in **R** space. The terms not written out in (35) contain the third derivatives with respect to R, and terms equivalent to them from A_2 and A_4, the fifth derivatives with respect to R and terms equivalent to them from A_0 and A_6, etc. We introduce in lieu of $A_2(r, R)$ a new unknown function $Q_2(r, R)$ defined by the relation

$$A_2(r,R)=\frac{r^2}{8}\left(2g(r)+n\frac{\partial g(r)}{\partial n}\right)\left(g''(R)-\frac{1}{R}g'(R)\right)+5Q_2(r,R). \quad (36)$$

Substituting in (35) the expressions (18), (27), and (36) and solving it with respect to the terms containing Q_2, we obtain

$$\frac{\partial Q_2(r,R)}{\partial R}+\frac{3}{R}Q_2(r,R)=\frac{\partial}{\partial R}\left\{3\tilde{Q}_1(r,R)-\frac{1}{2}Q_0(r,R)\right\}+\ldots, \quad (37)$$

were we introduced for convenience the function $\tilde{Q}_1$ in place of Q_1 in accordance with (29). At $R\gg r$ this equation has an asymptotic solution satisfying the condition $Q_2(r, \infty) = 0$, namely

$$Q_2(r,R)=\frac{a(r)}{R^3}+\frac{1}{R^3}\int_\infty^R y^3\frac{\partial}{\partial y}\left\{3\tilde{Q}_1(r,y)-\frac{1}{2}Q_0(r,y)\right\}dy+\ldots. \quad (38)$$

The first term on the right-hand side corresponds to the solution of the homogeneous equation, and a(r) is a certain arbitrary function of r. The terms not written out contain corrections of higher order of smallness to the solution of the homogeneous equation, and the terms of order of smallness A_4/R^2 and of higher order form the solution of the inhomogeneous equation. It is natural to assume that as $R\to\infty$ the order of smallness of the term A_4 in the series (7) is higher than the order of smallness of the term A_0 (i.e., $g(R) - 1$, according to (18)), and therefore all the terms that matter at large R have been taken into account in (38).

The integral term in (38), according to the foregoing estimates for Q_0 and $\tilde{Q}_1$, decreases with increasing R more rapidly than R^{-3}, and we integrate over all of **R** space. The degree of arbitrariness due to the first term in the right-hand side of (38) cannot be eliminated within the framework of our analysis. It can be noted, however, that this term has arisen purely formally during the course of the solution of (37), and for this reason it would appear in the asymptotic form of the function A_2 also far from the critical point, actually representing the long-range correlations that are immaterial here. It can therefore be assumed that the appearance of this term in (38) is accidental and does not reflect the real properties of the critical correlations; in a more rigorous theory it would be necessary to put $a(r) = 0$. Thus, the long-range behavior of the function $A_2(r, R)$ near the critical point is determined mainly by the first term in the right-hand side of (36). It is usually assumed that at large R we have at the critical point

$$g(R)-1\approx z(\ln R)/R^{1+\beta},\quad 0\leqslant\beta<1, \quad (39)$$

where z(ln R) is a slowly varying function of R (or a constant). Therefore the integrability or non-integrability of the function $A_2(r, R)$ over all of **R** space is determined by whether $\beta > 0$ or $\beta = 0$, respectively, if we assume $a(r) = 0$ in (38). We note also that when $\beta = 0$ the first terms in the right-hand sides of (36) and (38) turn out to be of the same order of smallness, and the question of whether it is necessary to retain in (38) the term a/R^3 is immaterial.

6. CORRELATION OF FLUCTUATIONS OF THE PARTICLE-NUMBER DENSITY AND OF THE STRESS TENSOR COMPONENTS

By way of an example, of the application of the obtained estimates, let us discuss the correlations of the simultaneous fluctuations of the particle-number density and of the elastic stress tensor components, particularly of the pressure near the critical point. The elastic stress tensor in the liquid model defined by the Hamiltonian (1) is represented by the dynamic variables[5]

$$\Pi^{\alpha\beta}(\mathbf{r}')=\sum_j\left\{\frac{p_j^\alpha p_j^\beta}{m}-\frac{1}{2}\sum_{j\neq l}\Phi'(|\mathbf{R}_j-\mathbf{R}_l|)\right.\times\left.\frac{(\mathbf{R}_j-\mathbf{R}_l)^\alpha(\mathbf{R}_j-\mathbf{R}_l)^\beta}{|\mathbf{R}_j-\mathbf{R}_l|}D(\mathbf{r}';\mathbf{R}_j-\mathbf{R}_l)\right\}\delta(\mathbf{r}'-\mathbf{R}_j), \tag{40}$$

where α and β are the indices of the Cartesian components and $D(\mathbf{r}, \mathbf{R})$ is a scalar operating acting on functions of r in accordance with the law

$$D(\mathbf{r};\mathbf{R})F(\mathbf{r})=\int_0^1 F(\mathbf{r}+\lambda\mathbf{R})\,d\lambda. \tag{41}$$

For the equilibrium mean value $\Pi^{\alpha\beta}(\mathbf{r}')$ we obtain from (2) and (40) $\langle\Pi^{\alpha\beta}(\mathbf{r}')\rangle = p\delta_{\alpha\beta}$, as we should. We multiply (20) by (40), average with the aid of the distribution functions $F_1(\mathbf{R}_1) = 1$, $F_2(\mathbf{R}_1, \mathbf{R}_2) = g(|\mathbf{R}_1 - \mathbf{R}_2|)$, $F_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = F_3(\mathbf{R}_3 - \mathbf{R}_1, \mathbf{R}_2 - \mathbf{R}_1)$, and subtract from the result the product of the mean values $np\delta_{\alpha\beta}$. Cumbersome calculations in which (2) is used lead to the expression

$$\langle\Delta n(\mathbf{r})\Delta\Pi^{\alpha\beta}(\mathbf{r}+\mathbf{R})\rangle=nkT(\delta(\mathbf{R})+n(g(R)-1))\delta_{\alpha\beta}+\frac{\mathbf{R}^\alpha\mathbf{R}^\beta}{R^4}n^2\int_\infty^R\Phi'(\rho)g(\rho)\rho^2\,d\rho-\frac{n^3}{2}\int\Phi'(\rho)\frac{\rho^\alpha\rho^\beta}{\rho}\left[\int_0^1(F_3(\rho,\mathbf{R}+\lambda\rho)-g(\rho))\,d\lambda\right]d\rho. \tag{42}$$

Let us examine separately the diagonal part and the deviator of the obtained tensor. In the former case, putting $\Pi^{\alpha\alpha}(\mathbf{r}') = \Pi(\mathbf{r}')$, adding and subtracting the function $F_3(\rho, R, \cos\vartheta)$ under the integral sign in the last term of (42), and using expressions (7) and (18) for the difference $F_3(\rho, R, \cos\vartheta) - g(\rho)$, we obtain

$$\frac{1}{3}\langle\Delta n(\mathbf{r})\Delta\Pi(\mathbf{r}+\mathbf{R})\rangle=nkT\delta(\mathbf{R})+n^2\left(\frac{\partial p}{\partial n}\right)_T(g(R)-1)+\frac{n^2}{3R^2}\int_\infty\Phi'(\rho)g(\rho)\rho^2\,d\rho-\frac{n^3}{6}\int\rho\Phi'(\rho)Q_0(\rho,R)\,d\rho-\frac{n^3}{6}\int\rho\Phi'(\rho)\left[\int_0^1(F_3(\rho,\mathbf{R}+\lambda\rho)-F_3(\rho,\mathbf{R}))\,d\lambda\right]d\rho. \tag{43}$$

In the derivation we used also expressions (2) and (5). To separate the possible long-range contributions made to this expression by the last term, we expand the integrand in (41) in a Taylor series in λ, which leads to an expansion of the operator $D(\mathbf{r}, \mathbf{R})$ in powers of $\partial/\partial\mathbf{r}$. Further calculations lead to the estimate

$$-\frac{n^3}{6}\int\rho\Phi'(\rho)\left[\int_0^1(F_3(\rho,\mathbf{R}+\lambda\rho)-F_3(\rho,\mathbf{R}))\,d\lambda\right]d\rho=\frac{n^3}{216}\int\rho^3\Phi'(\rho)\left(2g(\rho)+n\frac{\partial g(\rho)}{\partial n}\right)d\rho\cdot\Delta_{\mathbf{R}}g(R)+\ldots, \tag{44}$$

where the omitted terms have at large R are of the order of smallness $g^{IV}(R)$, $\partial^2 Q_0/\partial^2 R$, $\partial Q_1/\partial R$, $\partial^2 Q_2/\partial R^2$, etc. Taking into account all the foregoing estimates, we see that near the critical point the long-range contributions to the correlation function (43) are equal to

$$\frac{1}{3}\langle\Delta n(\mathbf{r})\Delta\Pi(\mathbf{r}+\mathbf{R})\rangle\sim n^2\left(\frac{\partial p}{\partial n}\right)_T(g(R)-1)+\frac{n^3}{216}\int\rho^3\Phi'(\rho)\left(2g(\rho)+n\frac{\partial g(\rho)}{\partial n}\right)d\rho\cdot\Delta_{\mathbf{R}}g(R)+\ldots. \tag{45}$$

At the critical point itself, however, the coefficient of the first term in the right-hand side of (45) vanish, and on the while this term is integrable over all of **R** space, as is clear from (4), in all states of the system, including the critical point. The second term in (45) decreases with increasing R more rapidly than R^{-3} at any permissible value of β in (39). Thus, the correlation function (43) contains "moderately long-range" contributions, which are, however, integrable at the critical point.

If we define the fluctuations of the thermodynamic pressure by

$$\Delta p=\frac{1}{3V}\int_{(V)}\Delta\Pi(r)\,dr, \tag{46}$$

where V is a certain large volume, then double integration of (43) with respect to **r** and **R** within this volume, using Eqs. (2), (4), and (5), yields

$$\langle\Delta N\Delta p\rangle=nkT, \tag{47}$$

which coincides with the result of the thermodynamic theory of fluctuations that are not sensitive to the critical point.

We consider now the deviator of the tensor (42). We put $\mathring{\Pi}^{\alpha\beta}(\mathbf{r}) = \Pi^{\alpha\beta}(\mathbf{r}) - \frac{1}{3}\Pi(\mathbf{r})\delta_{\alpha\beta}$. Repeating the arguments given above, we obtain now in place of (43)

$$\langle\Delta n(\mathbf{r})\Delta\mathring{\Pi}^{\alpha\beta}(\mathbf{r}+\mathbf{R})\rangle=\left\{\frac{n^2}{R^2}\int_\infty^R\Phi'(\rho)g(\rho)\rho^2\,d\rho-\frac{n^3}{240}\int\rho^3\Phi'(\rho)\left(2g(\rho)+n\frac{\partial g(\rho)}{\partial n}\right)d\rho\left(g''(R)-\frac{1}{R}g'(R)\right)-\frac{n^3}{6}\int\rho\Phi'(\rho)Q_2(\rho,R)\,d\rho\right\}\left(\frac{\mathbf{R}^\alpha\mathbf{R}^\beta}{R^2}-\frac{1}{3}\delta_{\alpha\beta}\right)-\frac{n^3}{2}\int\rho\Phi'(\rho)\left(\frac{\rho^\alpha\rho^\beta}{\rho^2}-\frac{1}{3}\delta_{\alpha\beta}\right)\left[\int_0^1(F_3(\rho,\mathbf{R}+\lambda\rho)-F_3(\rho,\mathbf{R}))\,d\lambda\right]d\rho. \tag{48}$$

An estimate of the long-range contributions from the last integral, obtained by the same method as above, leads to a general estimate for large R:

$$\langle\Delta n(\mathbf{r})\Delta\mathring{\Pi}^{\alpha\beta}(\mathbf{r}+\mathbf{R})\rangle\approx\frac{n^3}{6}\left\{\frac{1}{120}\int\rho^3\Phi'(\rho)\left(2g(\rho)+n\frac{\partial g(\rho)}{\partial n}\right)d\rho\left(g''(R)-\frac{1}{R}g'(R)\right)-\frac{1}{R^3}\int\rho\Phi'(\rho)a(\rho)\,d\rho\right\}\times\left(\frac{\mathbf{R}^\alpha\mathbf{R}^\beta}{R^2}-\frac{1}{3}\delta_{\alpha\beta}\right)+\ldots. \tag{49}$$

We have thus obtained moderately-long-range contributions to this correlation function at the critical point, if $a(r) = 0$ in (38). On the other hand, if $a(r) \neq 0$, or if $\beta = 0$ in (39), then the right-hand side of (49) decreases like R^{-3} at the critical point.

If we define the fluctuations of the macroscopic shear stresses by means of

$$\Delta\mathring{\sigma}^{\alpha\beta}=\frac{1}{V}\int_{(V)}\Delta\mathring{\Pi}^{\alpha\beta}(\mathbf{r})\,dr, \tag{50}$$

in analogy with (46), then we obtain from (43) and (47) the exact result

$$\langle \Delta N \Delta \mathring{\sigma}^{\alpha\beta} \rangle = 0, \qquad (51)$$

in the spirit of the thermodynamic theory of fluctuations. It is interesting to note, however, that the "density" of these fluctuations, defined by (48), does not vanish identically.

7. DISCUSSION OF RESULTS

We introduce the notation

$$A_l(r, R) = (2l+1) Q_l(r, R), \quad l \geqslant 3. \qquad (52)$$

Then expression (7), (18), (27), and (36) taken together yield at large values of R

$$F_3(r, R, \cos\vartheta) = g(r) + \left(2g(r) + n\frac{\partial g(r)}{\partial n}\right)\left\{g(R) - 1 - \frac{r}{2}g'(R)\cos\vartheta \right. \qquad (53)$$

$$\left. + \frac{r^2}{16}\left(g''(R) - \frac{1}{R}g'(R)\right)(3\cos^2\vartheta - 1)\right\} + \sum_{l=0}^{\infty}(2l+1)Q_l(r, R)P_l(\cos\vartheta).$$

The separated second term in the right-hand side contains all the most important long-range and moderately-long-range contributions to the three-particle correlation function of a classical liquid near the critical point and at the point itself, if $a(r) = 0$ in (38). Otherwise an additional term $5a(r)/R^3$ appears in the curly brackets of (53). Estimates for the functions Q_0, Q_1, and Q_2 were given above. If $a(r) = 0$, then all are integrable over all of **R** space in all states of the system, including the cri critical point. It is difficult to estimate the rate of decrease of the remaining functions $Q_l(r, R)$ with $l \geq 3$ as R increases. Under the natural assumption that the order of smallness of the sequence $A_0, A_2, A_4, \ldots$ from (7) at least does not decrease in any interval of the indices with increasing R, then it turns out that the second term of (53) contains not only the most important long-range contribution, but all the existing ones.

Notice should be taken of the very special form of the slowly-decreasing contributions for the function $F_3(r, R, \cos\vartheta)$ as $R \to \infty$ at the critical point according to (53). This makes the frequently employed various approximations of the function F_3 unsuitable. For example, Kirkwood's well-known approximation

$$F_3{}^s(\mathbf{r}, \mathbf{R}) \approx g(r)g(R)g(|\mathbf{R} - \mathbf{r}|) \qquad (54)$$

leads to an incorrect result even in the principal term of the asymptotic expansion for $F_3(\mathbf{r}, \mathbf{R}) - g(r)$ as $R \to \infty$, which is proportional to $g(R) - 1$.

If we confine ourselves in (53) to the principal term of the asymptotic estimate, containing no angular dependences, then the remaining equation satisfies the assumption of the "contraction of the correlations" from[1] and agrees with the hypothesis of conformal invariance from[6].

Since equations of the Schofield type (16) can be derived also for other systems, for example the Ising model and others, it is very probable that exact asymptotic estimates for three-particle correlations near second-order phase transition points can be obtained also in those cases. In addition, for a classical liquid near the critical point, and apparently also for other system, a similar analysis of the more interesting long-range four-particle correlations is possible. We shall devote a separate article to this last problem.

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