
NON-GAUSSIAN CONTRIBUTIONS TO THERMODYNAMIC FLUCTUATIONS

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Gibbs' statistical distributions have been used to analyze the third- and fourth-order fluctuation moments of volume, energy, and particle number. In contrast to the Gaussian model, the third moments do not vanish, and the fourth ones include extra non-Gaussian terms. For the van der Waals equation of state, the third moments and the Gaussian contributions to the fourth moments reveal a similar temperature dependence along the critical isochore — they are proportional to the isothermal compressibility squared. The moments of particle number fluctuations behave in this way near the critical isochore. The non-Gaussian contributions to the fourth moment of these fluctuations increase at a higher rate as the critical point (CP) is approached, but remain negligible at temperatures currently reachable.

Introduction

In the analysis of the molecular light scattering in fluids in a non-critical region, it is sufficient to restrict consideration to the single scattering, whose intensity is determined by the second correlation moments of fluctuations. The last are well investigated [1–3]; they are expressed through such thermodynamic parameters as the compressibility, heat capacity, and thermal expansion coefficient of the substance. As CP is approached, both fluctuations and the correlation length r_c between them increase. As a result, the role of the scattering effects of higher multiplicities, whose intensities are determined by the higher moments of fluctuations, becomes appreciable (see, e.g., [4]).

The double scattering is most investigated [4–6]. Its analysis is usually performed with the use of the Gaussian statistics of fluctuations, within the framework of which the moments of even orders reduce to a sum of

products of pair moments (Wick's theorem), and odd moments are identically zero. As a result, the scattering effects of second and higher multiplicities carry no new information about the substance, but are parasitic against the background of the single scattering; effects of fractional multiplicities are absent at all.

The applicability of the Gaussian approximation to the analysis of the double scattering is based on the replacement of the four-point correlation function (CF) for density fluctuations (hereinafter, we shall speak about CP in a liquid - vapor system) by its asymptotic expressions [7,8] for the situation where one pair of scattering centers is separated from the other by a distance $r \gg \lambda > r_c$ ($\lambda \approx 5 \cdot 10^{-5}$ cm is the length of a light wave in the medium). Such a replacement really works in the hydrodynamic region ($r_c \ll \lambda$), which corresponds to the temperature interval $\tau \equiv |T - T_c|/T_c \geq 10^{-4}$ and is typical of the majority of actual experiments. It is impossible, however, to apply similar asymptotes [7–9] for the three-point CF to the analysis of the so-called interference scattering of multiplicity 1.5 in the above temperature interval, because all the three scattering centers are the distance $r \leq r_c \ll \lambda$ apart from one another.

In the present paper, an attempt to go beyond the limits of the Gaussian model of fluctuations and to explore the third and fourth correlation moments of fluctuations of volume, energy, and particle number without use of the perturbation theory is made. The relation of these moments to the thermodynamic parameters of the substance and their derivatives is established. For fluctuations of the volume and the

energy, a temperature behavior of the non-Gaussian contributions is analyzed with the help of the van der Waals equation. The structure of the third and fourth correlation moments of fluctuations of the particle number (of the density) appears most simple — they are expressed only through the isothermal compressibility of the substance and can be analyzed in the region close to CP. The possibility of experimental observation of non-Gaussian fluctuations by the method of molecular light scattering in fluids is considered.

1. General Formulae

The higher correlation moments can be calculated in two ways: 1) directly with the help of statistical sums or distribution functions for a macroscopic system that is a small part of another large closed system (the medium); 2) in the framework of the quasi-thermodynamic fluctuation theory by Einstein, but without changing to series expansions typical of the Gaussian model. The both approaches are realized to a certain extent in papers [10, 11]. In particular, it was shown that all the moments of fluctuations of extensive thermodynamic quantities are equal in both approaches, and that the form of pair moments is the same as that within the Gaussian approach. But no detailed analysis of higher-order moments was carried out.

Consider a system with a fixed mole number N of a substance whose energy and volume fluctuate about their equilibrium values E and V . It is convenient to calculate the fluctuations ΔE and ΔV using the isothermal-isobaric ensemble, in which the probability dw_{nv} of that the system has a volume within an interval $(v, v + dv)$ and is in a quantum state of energy e_{nv} is given by [2]

$$dw_{nv} = \frac{1}{Q} \exp\left(-\frac{e_{nv} + Pv}{kT}\right) dv, \quad (1)$$

where T and P are the temperature and pressure of the medium, which equal the equilibrium values of the temperature and pressure of the system, k is the Boltzmann constant, and the statistical integral $Q = \int dv \sum_n \exp\left(-\frac{e_{nv} + Pv}{kT}\right)$ satisfies the relation

$$k \ln Q = S(E, V) - \frac{1}{T}E - \frac{P}{T}V. \quad (2)$$

Following [10, 11], we consider the right-hand part of formula (2) as the Legendre transform $S(F_1, F_2) = S(X_1, X_2) - F_1 X_1 - F_2 X_2$ for the equilibrium entropy of the system, with the help of which the change from the

set of extensive variables $E \equiv X_1$ and $V \equiv X_2$ to that of intensive variables $F_1 \equiv 1/T$ and $F_2 \equiv P/T$ is realized. We have $(dS(F_1, F_2))_N = -X_1 dF_1 - X_2 dF_2$, whence

$$X_1 = -\left(\frac{\partial S}{\partial F_1}\right)_{F_2, N}, \quad X_2 = -\left(\frac{\partial S}{\partial F_2}\right)_{F_1, N}. \quad (3)$$

Formula (1) takes the form

$$dw_{nv} = \exp\left(-\frac{S(F_1, F_2) + F_1 e_{nv} + F_2 v}{k}\right) dv, \quad (4)$$

and, thus, the mean values

$$X_1 = \sum_n \int e_{nv} dw_{nv}, \quad X_2 = \sum_n \int v dw_{nv} \quad (5)$$

are functions of the variables F_i .

It is easy to verify that the first correlation moments for the fluctuations of the energy $\Delta E = e_{nv} - X_1 \equiv \Delta x_1$ and the volume $\Delta V = v - X_2 \equiv \Delta x_2$ equal zero. Taking into account this circumstance, as well as formulae (3) and (4), we determine the second and higher correlation moments by differentiating (5) with respect to the variables F_i . We get ($i, j, k, l = 1, 2$)

$$\langle \Delta x_i \Delta x_k \rangle = -k \left(\frac{\partial X_i}{\partial F_k}\right), \quad (6)$$

$$\langle \Delta x_i \Delta x_j \Delta x_k \rangle = k^2 \left(\frac{\partial^2 X_i}{\partial F_j \partial F_k}\right), \quad (7)$$

$$\begin{aligned} \langle \Delta x_i \Delta x_j \Delta x_k \Delta x_l \rangle = \\ = -k^3 \left(\frac{\partial^3 X_i}{\partial F_j \partial F_k \partial F_l}\right) + k^2 \left(\frac{\partial X_i}{\partial F_l}\right) \left(\frac{\partial X_j}{\partial F_k}\right) + \\ + k^2 \left(\frac{\partial X_j}{\partial F_l}\right) \left(\frac{\partial X_i}{\partial F_k}\right) + k^2 \left(\frac{\partial X_k}{\partial F_l}\right) \left(\frac{\partial X_i}{\partial F_j}\right), \end{aligned} \quad (8)$$

where the differentiation with respect to the variable F_1 is carried out as the value of F_2 is kept fixed (and vice versa), and so is the value of N .

Formulas (6)–(8) completely coincide with analogous expressions previously obtained in [10, 11]. They can be used when other extensive parameters, e. g. the mole numbers N_i of different components, fluctuate in addition to the internal energy and the volume. The variables $F_{i+2} = -\mu_i/T$, μ_i being the chemical potential of the i -component, are then the corresponding intensive parameters.

2. The Explicit Form of Correlation Moments

In the following calculations, it is convenient to use the relations

$$\begin{aligned} \left(\frac{\partial A}{\partial F_1}\right)_{F_2, N} &= -TP \left(\frac{\partial A}{\partial P}\right)_{T, N} - T^2 \left(\frac{\partial A}{\partial T}\right)_{P, N}, \\ \left(\frac{\partial A}{\partial F_2}\right)_{F_1, N} &= T \left(\frac{\partial A}{\partial P}\right)_{T, N}, \end{aligned} \quad (9)$$

where A is the parameter X_i or its derivative with respect to temperature or pressure. They are easily proved using the method of jacobians.

For the second moments (7), using (9), we get (hereinafter, we omit the subscript N at derivatives)

$$\langle(\Delta V)^2\rangle = -kT \left(\frac{\partial V}{\partial P}\right)_T = kTV \beta_T, \quad (10)$$

$$\begin{aligned} \langle\Delta V \Delta E\rangle &= kTP \left(\frac{\partial V}{\partial P}\right)_T + kT^2 \left(\frac{\partial V}{\partial T}\right)_P = \\ &= -kTPV \beta_T - kT^2V \alpha_P, \end{aligned} \quad (11)$$

$$\begin{aligned} \langle(\Delta E)^2\rangle &= kTP \left(\frac{\partial E}{\partial P}\right)_T + kT^2 \left(\frac{\partial E}{\partial T}\right)_P = \\ &= kTP^2V \beta_T - 2kT^2PV \alpha_P + kT^2Nc_P, \end{aligned} \quad (12)$$

where β_T , α_P , and c_P denote, respectively, the isothermal compressibility, thermal expansion coefficient, and molar heat capacity at a constant pressure of the system. These results coincide with the corresponding formulas of the Gaussian model [1,2]. The discrepancies arise for the higher correlation moments.

In particular, the third moments differ from zero. We have

$$\langle(\Delta V)^3\rangle = k^2T^2 \left(\frac{\partial^2 V}{\partial P^2}\right)_T, \quad (13)$$

$$\begin{aligned} \langle(\Delta V)^2 \Delta E\rangle &= \\ &= -k^2T^2 \left[\left(\frac{\partial V}{\partial P}\right)_T + P \left(\frac{\partial^2 V}{\partial P^2}\right)_T + T \left(\frac{\partial^2 V}{\partial T \partial P}\right) \right], \end{aligned} \quad (14)$$

$$\begin{aligned} \langle\Delta V (\Delta E)^2\rangle &= k^2T^2 \left[2P \left(\frac{\partial V}{\partial P}\right)_T + P^2 \left(\frac{\partial^2 V}{\partial P^2}\right)_T + \right. \\ &\left. + 2TP \left(\frac{\partial^2 V}{\partial T \partial P}\right) + 2T \left(\frac{\partial V}{\partial T}\right)_P + T^2 \left(\frac{\partial^2 V}{\partial T^2}\right)_P \right], \end{aligned} \quad (15)$$

where mixed derivatives are calculated by the standard rule: the differentiation with respect to one variable is carried out by keeping the values of the other variables fixed.

The formula for $\langle(\Delta E)^3\rangle$ is obtained from (15) by substituting E for V . After some transformations, we can also write

$$\begin{aligned} \langle(\Delta E)^3\rangle &= k^2T^2 \left[2T \left(\frac{\partial E}{\partial T}\right)_P + T^2 \left(\frac{\partial^2 E}{\partial T^2}\right)_P - \right. \\ &- 4TP \left(\frac{\partial V}{\partial T}\right)_P - 2T^2P \left(\frac{\partial^2 V}{\partial T^2}\right)_P - 3P^2 \left(\frac{\partial V}{\partial P}\right)_T - \\ &\left. - 3TP^2 \left(\frac{\partial^2 V}{\partial T \partial P}\right) - P^3 \left(\frac{\partial^2 V}{\partial P^2}\right)_T \right]. \end{aligned} \quad (16)$$

It is convenient to represent the fourth moments (8) in the following form:

$$\begin{aligned} \langle\Delta x_i \Delta x_j \Delta x_k \Delta x_l\rangle &= \\ &= -k^3 \left(\frac{\partial^3 X_i}{\partial F_j \partial F_k \partial F_l} \right) + \langle\Delta x_i \Delta x_j\rangle \langle\Delta x_k \Delta x_l\rangle + \\ &+ \langle\Delta x_i \Delta x_k\rangle \langle\Delta x_j \Delta x_l\rangle + \langle\Delta x_i \Delta x_l\rangle \langle\Delta x_j \Delta x_k\rangle. \end{aligned} \quad (17)$$

Without the first term on the left-hand side, they would reduce to a sum of all the possible products of second moments, Wick's theorem being satisfied. It follows that this term is of a non-Gaussian origin.

The results of calculations for the non-Gaussian contributions to the fourth moments are as follows:

$$\langle(\Delta V)^4\rangle_{\text{nG}} = -k^3T^3 \left(\frac{\partial^3 V}{\partial P^3}\right)_T, \quad (18)$$

$$\begin{aligned} \langle(\Delta V)^3 \Delta E\rangle_{\text{nG}} &= \\ &= k^3T^3 \left[2 \left(\frac{\partial^2 V}{\partial P^2}\right)_T + T \left(\frac{\partial^3 V}{\partial P^2 \partial T}\right) + P \left(\frac{\partial^3 V}{\partial P^3}\right)_T \right], \end{aligned} \quad (19)$$

$$\begin{aligned} \langle(\Delta V)^2 (\Delta E)^2\rangle_{\text{nG}} &= \\ &= -k^3T^3 \left[2 \left(\frac{\partial V}{\partial P}\right)_T + 4T \left(\frac{\partial^2 V}{\partial T \partial P}\right) + 4P \left(\frac{\partial^2 V}{\partial P^2}\right)_T + \right. \\ &\left. + T^2 \left(\frac{\partial^3 V}{\partial P \partial T^2}\right) + 2TP \left(\frac{\partial^3 V}{\partial P^2 \partial T}\right) + P^2 \left(\frac{\partial^3 V}{\partial P^3}\right)_T \right], \end{aligned} \quad (20)$$

$$\langle\Delta V (\Delta E)^3\rangle_{\text{nG}} =$$

$$\begin{aligned}
 &= k^3 T^3 \left[6T \left(\frac{\partial V}{\partial T} \right)_P + 6P \left(\frac{\partial V}{\partial P} \right)_T + 6T^2 \left(\frac{\partial^2 V}{\partial T^2} \right)_P + \left(\frac{\partial^2 \omega}{\partial \tau^2} \right)_\pi = -\frac{64f^2 (g'' + 6g'f)}{(g' + 24\tau f^2)^3}, \right. \\
 &+ 12TP \left(\frac{\partial^2 V}{\partial P \partial T} \right) + 6P^2 \left(\frac{\partial^2 V}{\partial P^2} \right)_T + T^3 \left(\frac{\partial^3 V}{\partial T^3} \right)_P + \left(\frac{\partial^2 \omega}{\partial \pi \partial \tau} \right) = \frac{8f (g'' + 3g'f - 72\tau f^3)}{(g' + 24\tau f^2)^3}, \\
 &+ 3TP^2 \left(\frac{\partial^3 V}{\partial P^2 \partial T} \right) + 3T^2 P \left(\frac{\partial^3 V}{\partial P \partial T^2} \right) + P^3 \left(\frac{\partial^3 V}{\partial P^3} \right)_T \left. \right) \cdot (21) \quad \left(\frac{\partial^3 \omega}{\partial \pi^3} \right)_\tau = \frac{g''' + 1296\tau f^4}{(g' + 24\tau f^2)^4} - \frac{3(g'' - 144\tau f^3)^2}{(g' + 24\tau f^2)^5}. \quad (23)
 \end{aligned}$$

The formula for $\langle (\Delta E)^4 \rangle_{\text{NG}}$ coincides with (21) if V is replaced by E in it.

Since

$$\begin{aligned}
 \frac{1}{V} \left(\frac{\partial^2 V}{\partial P^2} \right)_T &= \beta_T^2 - \left(\frac{\partial \beta_T}{\partial P} \right)_T, \\
 \frac{1}{V} \left(\frac{\partial^2 V}{\partial P \partial T} \right) &= -\alpha_P \beta_T - \left(\frac{\partial \beta_T}{\partial T} \right)_P,
 \end{aligned}$$

$$\left(\frac{\partial^2 E}{\partial T^2} \right)_P = N \left(\frac{\partial c_P}{\partial T} \right)_P - PV \alpha_P - PV \left(\frac{\partial \alpha_P}{\partial T} \right)_P \text{ etc.},$$

we see that the higher moments (13)–(21), having a rather intricate structure, are expressed through the same parameters β_T , α_P , and c_P as the second moments, and through their derivatives. It may be expected that they anomalously increase as CP is approached.

3. The Temperature Behavior of Higher Moments in the Frame of the van der Waals Model

The critical exponents of higher moments in the immediate vicinity of CP can be calculated using the scaling theory [3]. To analyze the behavior of higher moments in a wide temperature interval, we use the van der Waals equation represented in the following form:

$$\pi = 8\tau f(\omega) - g(\omega), \quad (22)$$

where $f(\omega) = 1/(3\omega + 2)$, $g(\omega) = 3\omega^3 / (3\omega + 2)(1 + \omega)^2$, and the dimensionless quantities $\pi = P/P_c - 1$, $\tau = T/T_c - 1$, and $\omega = V/V_c - 1$ characterize the proximity of the system to the critical state (above CP in the PV -diagram).

From formula (22), we find

$$\begin{aligned}
 \left(\frac{\partial \omega}{\partial \pi} \right)_\tau &= -\frac{1}{g' + 24\tau f^2}, \quad \left(\frac{\partial \omega}{\partial \tau} \right)_\pi = \frac{8f}{g' + 24\tau f^2}, \\
 \left(\frac{\partial^2 \omega}{\partial \pi^2} \right)_\tau &= \frac{-g'' + 144\tau f^3}{(g' + 24\tau f^2)^3},
 \end{aligned}$$

For the molar heat capacity of the van der Waals gas, we can write

$$\begin{aligned}
 c_P &= c_V - T \left(\frac{\partial V}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_V^2 = \\
 &= c_V + R(1 + \tau) \frac{24f^2}{g' + 24\tau f^2}, \quad (24)
 \end{aligned}$$

where we took into account that, for one mole, $P_c V_c / T_c = 3R/8$, R being the universal gas constant. The molar heat capacity c_V is a function of temperature alone; moreover, in a wide temperature interval, it may be considered as a constant.

Changing to the above dimensionless variables in formulas (10) - (16), taking into account that $g(0) = g'(0) = g''(0) = 0$, $g'''(0) = 9$, $f(0) = 1/2$, and using formulas (23), for the second moments on the critical isochore and for arbitrary values of τ , we obtain

$$\begin{aligned}
 \langle (\Delta V)^2 \rangle &= \frac{kTV_c}{6P_c} \tau^{-1}, \quad \langle \Delta V \Delta E \rangle = \frac{kTV_c}{2} \tau^{-1}, \\
 \langle (\Delta E)^2 \rangle &= \frac{3kTV_c P_c}{2} \tau^{-1} \left[1 + \frac{16c_V}{9R} \tau (1 + \tau) \right]. \quad (25)
 \end{aligned}$$

Under the same conditions, the third moments are equal to

$$\begin{aligned}
 \langle (\Delta V)^3 \rangle &= \frac{k^2 T^2 V_c}{12 P_c^2} \tau^{-2}, \\
 \langle (\Delta V)^2 \Delta E \rangle &= \frac{k^2 T^2 V_c}{12 P_c} \tau^{-2}, \\
 \langle \Delta V (\Delta E)^2 \rangle &= -\frac{k^2 T^2 V_c}{4} \tau^{-2}, \\
 \langle (\Delta E)^3 \rangle &= -\frac{9k^2 T^2 P_c V_c}{4} \tau^{-2} \times \\
 &\times \left[1 - \frac{64c_V}{27R} \tau^2 (1 + \tau) - \frac{32}{27R} \left(\frac{dc_V}{d\tau} \right) \tau^2 (1 + \tau)^2 \right]. \quad (26)
 \end{aligned}$$

Thus, the third moments are not only nonzero, but also increase faster ($\sim \tau^{-2}$) than the second moments (τ^{-1}) as CP is approached. It should be noted that the Gaussian contributions to the fourth moments have the same divergence. For instance, according to Wick's theorem, we have

$$\begin{aligned} \langle(\Delta V)^4\rangle_G &= \frac{k^2 T^2 V_c^2}{12 P_c^2} \tau^{-2}, \\ \langle(\Delta V)^3 \Delta E\rangle_G &= \frac{k^2 T^2 V_c^2}{4 P_c} \tau^{-2}, \\ \langle(\Delta V)^2 (\Delta E)^2\rangle_G &= \\ &= \frac{3k^2 T^2 V_c^2}{4} \tau^{-2} \left[1 + \frac{16c_V}{27R} \tau (1 + \tau) \right], \text{etc.} \end{aligned} \quad (27)$$

To estimate the temperature dependence of the non-Gaussian contributions to the fourth moments, consider just contribution (18). We have

$$\langle(\Delta V)^4\rangle_{nG} = \frac{k^3 T^3 V_c}{16 P_c^3} \tau^{-3} \left[1 - \frac{1}{9\tau} \right]. \quad (28)$$

We see that the Gaussian and non-Gaussian contributions to the fourth moments possess a significantly different temperature behavior. Far from CP, the Gaussian contribution is primary. As CP is approached, the non-Gaussian contribution increases faster (at first, as τ^{-3} , and then by a more complicated law). Having reached a maximum at $\tau = 4/27$, the non-Gaussian contribution decreases to zero and becomes negative at $\tau < 1/9$, increasing in modulus approximately as τ^{-4} , thus decreasing the total fourth moment. The relative value of the non-Gaussian contribution, when compared with the Gaussian contribution, equals $\left| \langle(\Delta V)^4\rangle_{nG} / \langle(\Delta V)^4\rangle_G \right| \cong kT_c / 12P_c V_c \tau^2 = 2/9N\tau^2$, where N is the total number of particles in the system. Formally, the both contributions become equal at $\tau^* \approx \sqrt{2/9N}$. Considering that light is scattered most efficiently by regions of linear size $\sim \lambda \approx 5 \cdot 10^{-5} \text{cm}$, and that the mean intermolecular distance $\approx 3 \cdot 10^{-8} \text{cm}$, we obtain that there are $\sim 5 \cdot 10^9$ particles in such a region, which corresponds to $\tau^* \approx 7 \cdot 10^{-6}$.

It is clear that the reliability of the given estimations is questionable for so small τ . The mean-field theory (the van der Waals equation is a variant of it) fails in this vicinity of CP, for Ginzburg's criterion $\tau \gg Gi$ is broken [3]. The manifestation of this fact is that for $\tau < \tau^*$, the total fourth moment becomes negative, which is impossible.

4. Fluctuations of the Number of Particles

We turn to consideration of the higher correlation moments of fluctuations of the particle number (of the density), which give the main contribution to the correlators of the permittivity fluctuations in fluids and eventually to the intensity of molecular light scattering in the critical region.

Assuming that a single-component system is in a thermostat and has a fixed volume V , we use the grand canonical ensemble. Following the approach of Section 1, we obtain

$$w_{n\tilde{N}} = \exp \left(- \frac{S(F_1, F_3) + F_1 e_{n\tilde{N}} + F_3 \tilde{N}}{k} \right) \quad (29)$$

for the distribution function, where $F_3 \equiv -\mu/T$ and $-(\partial S / \partial F_3)_{F_1, V} = N \equiv X_3$ is the average number of particles in the system. Differentiating the averages $X_1 = \sum_{n\tilde{N}} e_{n\tilde{N}} w_{n\tilde{N}}$, $X_3 = \sum_{n\tilde{N}} \tilde{N} w_{n\tilde{N}}$ with respect to the parameters F_1 and F_3 , we come to formulae (6)–(8) again, from which we get

$$\langle(\Delta N)^2\rangle = kT \left(\frac{\partial N}{\partial \mu} \right)_{T, V} = kTVn^2\beta_T, \quad (30)$$

$$\begin{aligned} \langle(\Delta N)^3\rangle &= k^2 T^2 \left(\frac{\partial^2 N}{\partial \mu^2} \right)_{T, V} = \\ &= k^2 T^2 V n^3 \left[2\beta_T^2 + \left(\frac{\partial \beta_T}{\partial P} \right)_{T, V} \right], \end{aligned} \quad (31)$$

$$\begin{aligned} \langle(\Delta N)^4\rangle &= k^3 T^3 \left(\frac{\partial^3 N}{\partial \mu^3} \right)_{T, V} + 3\langle(\Delta N)^2\rangle^2 = \\ &= k^3 T^3 V n^4 \left[6\beta_T^3 + 7\beta_T \left(\frac{\partial \beta_T}{\partial P} \right)_{T, V} + \left(\frac{\partial^2 \beta_T}{\partial P^2} \right)_{T, V} \right] + \\ &+ 3k^2 T^2 V^2 n^4 \beta_T^2, \end{aligned} \quad (32)$$

Here, we have used the formulae [2]

$$\left(\frac{\partial N}{\partial \mu} \right)_{T, V} = - \left(\frac{\partial P}{\partial V} \right)_{T, N}^{-1} \frac{N^2}{V^2},$$

$$\left(\frac{\partial P}{\partial \mu} \right)_{T, V} = \left(\frac{\partial P}{\partial \mu} \right)_{T, N} = \frac{N}{V},$$

and $n = N/V$ is the volume concentration of particles.

Although the non-Gaussian contribution [the first term in (32)] to the fourth moment increases faster than the Gaussian one (as β_T^3 and β_T^2 , respectively) as CP is approached, its relative value $|\langle(\Delta N)^4\rangle_{nG}/\langle(\Delta N)^4\rangle_G| \sim kT\beta_T/V \sim \tau^{-\gamma}/N$ becomes appreciable only at $\tau \sim 10^{-8}$ (it is assumed that the critical exponent of isothermal compressibility $\gamma \approx 5/4$) that is beyond the power of modern light scattering experiment. These results agree with estimations [5] obtained with the help of the asymptotes [7] for the four-point density CF.

The third (non-Gaussian) moment (31) has the same temperature behavior ($\sim \beta_T^2$) for $|\omega| \sim \tau$ as the Gaussian contributions to the fourth moment do. It is responsible for the sesquialteral molecular light scattering. In that temperature range where the correlation effects can be neglected, the relative magnitude of the contribution from the third moment to the fluctuations of permittivity ϵ , as compared to the corresponding contribution from the fourth moment (responsible for the double scattering), can be estimated using the relation

$$a \equiv \frac{\langle(\Delta\epsilon)^3\rangle}{\langle(\Delta\epsilon)^4\rangle} \approx \frac{(\partial\epsilon/\partial n)_T^3 \langle(\Delta n)^3\rangle}{(\partial\epsilon/\partial n)_T^4 \langle(\Delta n)^4\rangle} \sim \frac{1}{n(\partial\epsilon/\partial n)_T}. \quad (33)$$

Having calculated the derivative of ϵ with respect to the concentration, from the Clausius–Mossotti's law $(\epsilon - 1)/(\epsilon + 2) = An$ (A is a constant), we obtain $a \approx 1/(\epsilon + 2)(\epsilon - 1)$.

In the optical frequency range, $\epsilon \approx 2$ or lesser. In principle, we can find a substance for which a amounts to a considerable percent. The possible sesquialteral scattering will be masked by the double one, because both depend on the temperature similarly (as β_T^2). As a result, the problem of their separation, say, with the use of a proper geometry, arises. In actual experiments, this circumstance is ignored, since the sesquialteral scattering is considered to be negligible.

To calculate the intensity of the sesquialteral scattering in the hydrodynamic region in detail by the method of multiple scattering theory, the short-range peculiarities of the behavior of the propagator have to be analyzed, besides the moments themselves. The analysis is performed with the use of the theory of generalized

functions [12]. The pertinent results, together with a quantitative estimation of the intensity of the sesquialteral scattering, will be presented elsewhere.

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НЕГАУССОВІ ВНЕСКИ В ТЕРМОДИНАМІЧНІ ФЛУКТУАЦІЇ

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Резюме

За допомогою статистичних розподілів Гіббса проаналізовано треті і четверті кореляційні моменти флуктуацій об'єму, енергії та кількості частинок. На відміну від гауссової моделі треті моменти не дорівнюють нулю, а четверті містять додаткові негауссові члени. Для рівняння стану Ван-дер-Ваальса і на критичній ізохорі треті моменти та гауссові внески в четверті моменти мають однакову температурну залежність і пропорційні квадрату ізотермічної стисливості. Моменти флуктуацій кількості частинок ведуть себе аналогічно поблизу критичної ізохори. Негауссові внески в четвертий момент цих флуктуацій з наближенням до критичної точки зростають сильніше, але є нехтовно малими для нині доступних температур.