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Influence of Density Fluctuations on the Equation of State

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The influence of inhomogeneity of particle density on the equation of state has been considered in the approximation of homogeneous fluctuations. The formula for the relative mean square fluctuation has been derived taking into account intermolecular interaction. It has been shown that the density fluctuations cannot be neglected near the coexistence curve. This curve has been obtained without recourse to the Maxwell construction; unphysical parts of the van der Waals isotherms in fact never appear in the theory. Experimental parameters have not been used.

KEY WORDS: Equation of state; internal virial; density fluctuations; mean-square fluctuation; probability; probability distribution function; phase transition; isotherm; critical region.

1. INTRODUCTION

The equation of state for a fluid system containing N atoms (molecules) in volume V can be written in the general form$^{(1)}$

$$P = kT\rho + (W/3V) \tag{1}$$

where W is the internal virial and ρ denotes the density of particles. The form (1) can be regarded as the exact equation of state if the internal virial is calculated exactly. The proof of the last statement has been carried out in the

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case of the thermodynamic limit.(2) Since the exact partition function is not available in the theory, there is an enormously rich literature devoted to several approximations of Eq. (1). If the whole system is treated as a homogeneous one as far as the density is concerned, Eq. (1) always gives isotherms of the van der Waals type for temperatures below the critical one, independently of the accuracy to which the internal virial is calculated. Thus the Maxwell construction must be introduced ad hoc to correct an unphysical isotherm. Apart from the unphysical parts of the van der Waals isotherms, these isotherms lie above the experimental results and are too steep in the critical region. The best-known approximations of Eq. (1) connected with the so-called virial expansion, for which Mayer *et al.*(3) give the theoretical analysis, lead to rigorous results for states not too close to the critical region and do not remove all difficulties connected with the theory of condensation. One can become disillusioned with the series expansions since no general point of view emerges from them.

Our aim is to show in this paper the possibility of other approximations of Eq. (1). We shall reconsider the original idea conceived by Smoluchowski(4) that the density fluctuations should be taken into account in the derivation of the equation of state and are responsible for the phase transition. The density fluctuations are usually believed to be negligible from the macroscopic point of view. On the other hand, it is well known that the density fluctuations in a fluid system become abnormally large in the vicinity of the critical point and are responsible for the spectacular phenomenon of critical opalescence. We shall show in the next sections that taking into consideration the density fluctuations leads to the corrected equation of state and gives a phase transition analytically.

2. EQUATION OF STATE FOR INHOMOGENEOUS SYSTEM

Let us assume that as a result of interactions and the chaotic movement of atoms density fluctuations in a fluid system are created. We replace the actual inhomogeneous state of the system by an idealized model of inhomogeneity which consists in the division of the system into N_1 equal cells in which the number of particles differs from the mean number by plus or minus the root mean square fluctuation in the number of molecules. The starting point of our physical model consists in the observation that a fluid system near the critical state should show a "grainlike structure" since the deviation from the equilibrium value of density grows rapidly when the critical state is approached. Such a region, following Smoluchowski,(5) is treated as a subsystem in a reservoir. The subsystem is very small from a macroscopic point of view but sufficiently large to allow the application of statistical mechanics to describe the properties of the subsystem. From the phenomenon of critical opalescence one can deduce that in the volume of one cell of magnitude λ^3 (where λ is the wavelength of light) there are on the average 10^6–10^7 molecules. So we have the number of cells of the order 10^{15}–10^{16} in one mole of gas in the critical state. Such a "cell" model was introduced by Smoluchowski$^{(5)}$ and a similar model is described in Chapter 7 of Ref. 6. The subsystem remains in the nonequilibrium state with the reservoir but we can assume a local equilibrium.$^{(7)}$ In other words, it is generally postulated that all thermodynamic functions of state exist for each element (subsystem) of the system. These thermodynamic quantities are the same functions of the local state variables as the corresponding equilibrium thermodynamic quantities.$^{(8)}$ Thus the total internal virial for an inhomogeneous system can be expressed by a sum over virials of subsystems as follows:

$$W = \sum_{i=1}^{N_1} W_i + W_I \tag{2}$$

where W_I is related to the energy of interaction between subsystems. In the approximation of homogeneous fluctuations the internal virial of the ith subsystem can be expressed in the following form:

$$W_i = -\tfrac{1}{2}\rho_i n_i \bar{\omega} \tag{3}$$

where ρ_i and n_i denote density and number of particles in the fluctuation, respectively. The symbol $\bar{\omega}$ represents the intermolecular interaction

$$\bar{\omega} = \int_0^\infty r\frac{\partial U(r)}{\partial r}\, g(r)\, d^3\mathbf{r} \tag{4}$$

where $U(r)$ is the interaction potential and $g(r)$ denotes the equilibrium radial distribution function.

In the first approximation we introduced the mean value of ω equal to the equilibrium value of this quantity, assuming in this way that the dependence of the function $g(r)$ on density can be neglected in our considerations. One can say that we express the local virial in approximation to the first two terms in the virial expansion. Incidentally, this is the same level of approximation as the one given by the van der Waals equation.$^{(9)}$ The last assumption certainly changes the accuracy of the final results but neither the generality of our considerations nor the physical model.

A more detailed discussion of this problem is given in Section 5.

The relative fluctuation of density in the ith subsystem can be described by

$$\delta_i = (\rho_i - \rho_0)/\rho_0 \tag{5}$$

Using Eqs. (3) and (5), formula (2) can be rewritten in the form

$$W = -\tfrac{1}{2}\rho_0 n_0 \bar{\omega} \sum_{i=1}^{N_1} (1 + \delta_i)^2 + W_I \tag{6}$$

where n_0 is the equilibrium number of atoms in the volume of the subsystem. Since the total number of atoms N is constant, we can write

$$\sum_{i=1}^{N_1} \delta_i = 0 \tag{7}$$

Using Eq. (7) and replacing δ_i^2 by $\langle \delta^2 \rangle$ in Eq. (6), the total internal virial for an inhomogeneous gas system can be expressed in the following form:

$$W = -\tfrac{1}{2}\rho_0 N\bar{\omega}(1 + \langle \delta^2 \rangle) + W_I \tag{8}$$

Substituting (8) into (1), we obtain the following formula for the pressure in the total system:

$$P = kT\rho_0 - \tfrac{1}{6}\rho_0\bar{\omega}(1 + \langle \delta^2 \rangle) - akT\rho_0 \tag{9}$$

where we replaced the term $W_I/3V$ by $-akT\rho_0$. The undetermined parameter a satisfies the condition $a \ll 1$, since it can be assumed that the energy of interaction between subsystems is small. Thus, the correction given by the density fluctuations to the pressure of the system is $W_0\langle \delta^2 \rangle/3V - akT\rho_0$.

All subscripts "zero" used in this paper denote the equilibrium values.

3. MEAN SQUARE FLUCTUATION IN THE PARTICLE DENSITY

To calculate the mean square density fluctuation, we shall apply the method developed by Smoluchowski$^{(5)}$ for calculating the probability of occurrence of a fluctuation.

The general formula for the probability can be written as follows:

$$\rho(\delta)\, d\delta = C \exp[-L(\delta)/kT]\, d\delta \tag{10}$$

where $L(\delta)$ denotes the work necessary to create the subsystem reversibly from the state of equilibrium with the reservoir to the state described by the parameter δ. The work L done by the reservoir on the subsystem can be expressed by the net change of the proper thermodynamic potential of the whole system. Before we evaluate the formula (10) further we remark that the density fluctuations must obviously be independent of whether we consider fluctuations in the number of particles at constant volume or in volume at constant number of particles. In other words, it is inessential whether one chooses n or v as the independent variable. Thus, we can write

$$\bar{\delta} = \overline{\frac{\rho_i - \rho_0}{\rho_0}} = \overline{\frac{n_i - n_0}{n_0}}\bigg|_{v=\text{const}} = -\overline{\frac{v_i - v_0}{v_i}}\bigg|_{n=\text{const}} \tag{11}$$

and since the pressure is a function of ρ and T only, the following formula must be satisfied:

$$\left(\frac{\partial P}{\partial \rho}\right)_{T,N} = \left(\frac{\partial P}{\partial \rho}\right)_{T,V} \tag{12}$$

In the case of temperature and volume as the independent variables, the work L can be expressed by the change of the Helmholtz free energy. Since the volume of the reservoir is much larger than the volume of the subsystem, we can assume that the pressure in the reservoir remains constant and equal to the equilibrium value P_0 during the whole process when the fluctuation is being created. Thus, the work L can be expressed as follows:

$$L(\delta) = -\int_{v_0}^{v} (P - P_0)\, dv \tag{13}$$

with the temperature of the subsystem kept constant since the fluctuations in the temperature and density can be regarded as statistically independent.(7) In a first approximation the formula (13) can be replaced by (10)

$$L(\delta) = -\tfrac{1}{2}\, \Delta P\, \Delta v \tag{14}$$

where the values ΔP and Δv are related to the subsystem. There are a few ways of evaluating the formula (14) further, each of which leads in principle to the same result. One can, for instance, express the local pressure by the general formula (1) using the local variables. Then, the local, isothermal change of pressure due to the density fluctuation with the parameter δ will be

$$\Delta P = (kT - \tfrac{1}{3}\rho_0\bar{\omega})\rho_0\, \delta - \tfrac{1}{6}\rho_0\bar{\omega}\, \delta^2 \tag{15}$$

Instead of Δv we can write

$$\Delta v = (\partial P/\partial v)^{-1}\, \Delta P \tag{16}$$

Using Eqs. (13)–(16) and retaining terms with δ^2 only, we obtain

$$\langle \delta^2 \rangle = kT/n_0(kT - \tfrac{1}{3}\rho_0\bar{\omega}) \tag{17}$$

In the last equation the quantity n_0 remains a parameter of the theory. Although Eq. (17) formally holds for all values of n_0, only one value of n_0 has a physical meaning. One can express this value by $n_0 = N/N_1$, where the number N_1 has the physical meaning of the most probable number of fluctuations and at least in principle can be determined both theoretically and experimentally.

In the approximation of a homogeneous fluctuation some parameter characterizing the fluctuation (volume, number of particles, or number of fluctuations) must occur, but this parameter can be determined, e.g., from the condition(11)

$$\partial p(\delta)/\partial \xi = 0$$

which gives the most probable value for ξ, where ξ denotes one of the parameters mentioned above and characterizes the fluctuation.

4. DISCUSSION

It is evident from the formula (17) that the density fluctuations are really negligible for ideal or very dilute gas since $\langle\delta^2\rangle$ is of the order $O(n_0{}^{-1/2})$, i.e., $\langle\delta^2\rangle = 1/n_0$, when the internal virial is much smaller than the kinetic energy. The qualitative dependence of the internal virial on the density can be deduced from the form of the interaction potential and the radial distribution function. The value of $\rho_0\bar{\omega}$ is near zero when the density is small, but as one compresses the gas this value increases and reaches a maximum for some particular value of density. On further compressing the gas, the value $\rho_0\bar{\omega}$ decreases and for very high density can even be negative because of the dominance of the repulsive interaction. If the temperature of the system is not too high, the internal virial can be of the same order as the kinetic energy of a compressed gas or an extended liquid.

Considering Eq. (15), one can find

$$\delta_c = 6(kT - \tfrac{1}{3}\rho_0\bar{\omega})/\rho_0\bar{\omega} \tag{18}$$

since the value of δ for which the local change of pressure ΔP due to the density fluctuation is equal to zero. This change would be negative for $\delta > \delta_c$, which would mean negative compressibility. Even in a dilute gas system there is a finite probability that the fluctuation with high density corresponding to a liquid phase can be created in a small element of volume for a short period of time, since the probability distribution function (10) is determined for all values of δ even away from the critical region. Such states of high abnormality are well described in the literature.(12,13) The whole fluid system becomes unstable mechanically when the mean square fluctuation is equal to the square of the critical fluctuation defined by Eq. (18). Thus, we propose the criterion of stability in the general form

$$\langle\delta^2\rangle = \delta_c{}^2 \tag{19}$$

The stability criterion (19) describes the behavior of a subsystem and is connected with negative compressibility. It is worthwhile to mention that although the stability criterion for a representative subsystem decides about the stability of the whole system (unit volume of it), the overall static isothermal compressibility for the whole system need not be negative. Clearly, the local and overall compressibilities are different.(14) This results from the definition of the isothermal compressibility. The local isothermal compressibility can be found from Eq. (1) applied for an homogeneous subsystem, while the overall compressibility should be calculated from Eq. (9).

Now we shall turn to the problem of the limits of the integral in calculating the mean square fluctuation. Equation (17) was obtained from the formula

$$\langle\delta^2\rangle = \int_{-\infty}^{+\infty} \delta^2\rho(\delta)\, d\delta \bigg/ \int_{-\infty}^{+\infty} \rho(\delta)\, d\delta \tag{20}$$

The limits $\pm\infty$ in Eq. (20) can be assumed only for a very sharp, rapidly convergent probability distribution function. Thus formula (17) for the mean square fluctuation is applicable only for states away from the critical region. When the critical region is approached the probability distribution function becomes more and more flat because of the decrease of the probability index. The possible values of δ are physically limited and we should introduce these limits into equation (22). Since the parameter δ cannot be smaller than -1 [this results from the definition (5) of δ], the upper limit must be $+1$, since for any even probability distribution function the limits of the integral in the equation

$$\langle\delta\rangle = C\int_{\delta_{\min}}^{\delta_{\max}} \delta\rho(\delta)\, d\delta \equiv 0 \tag{21}$$

must be the same. Otherwise $\langle\delta\rangle$ would not be equal to zero. Such a result would be justified only in the case of creation or annihilation of particles. Thus, the mean square fluctuation can be expressed by the formula

$$\langle\delta^2\rangle = \int_{-1}^{+1} \delta^2 \exp\left(-\frac{n_0}{2kT}\,\alpha\delta^2\right) d\delta \bigg/ \int_{-1}^{+1} \exp\left(-\frac{n_0}{2kT}\,\alpha\delta^2\right) d\delta \tag{22}$$

where $\alpha = kT - \frac{1}{3}\rho_0\bar{\omega}$. From Eq. (22) we obtain

$$\langle\delta^2\rangle = \frac{kT}{n_0\alpha}\left[1 - \frac{2\exp(-n_0\alpha/2kT)}{(2\pi kT/n_0\alpha)^{1/2}\phi([n_0\alpha/2kT]^{1/2})}\right]$$

where $\phi(z)$ denotes the probability integral. The last equation can be rewritten as follows:

$$\langle\delta^2\rangle = \frac{kT}{n_0\alpha}\left[1 - \frac{\exp(-n_0\alpha/2kT)}{{}_1F_1(\frac{1}{2};\,\frac{3}{2};\,-n_0\alpha/2kT)}\right]$$

where ${}_1F_1(\beta;\gamma;z)$ denotes the confluent hypergeometric function. Because of the identity ${}_1F_1(\beta;\gamma;z) = e^z\,{}_1F_1(\gamma-\beta;\gamma;-z)$, we can express the mean square fluctuation in the form

$$\langle\delta^2\rangle = (kT/n_0\alpha)\{1 - [{}_1F_1(1;\,\tfrac{3}{2};\,n_0\alpha/2kT)]^{-1}\} \tag{23}$$

Substituting (18) and (23) into (19), we obtain the following equation:

$$\frac{36\alpha^2}{(\rho_0\bar{\omega})^2} = \frac{kT}{n^0\alpha}\left\{1 - \left[{}_1F_1\left(1;\frac{3}{2};\frac{n_0\alpha}{2kT}\right)\right]^{-1}\right\}$$

which leads to the equation

$$kT = \frac{1}{3}\rho_0\overline{\omega} + {n_0}^{-1/3}\left(\frac{kT(\rho_0\overline{\omega})^2}{36}\left\{1 - \left[{}_1F_1\left(1;\frac{3}{2};\frac{n_0\alpha}{2kT}\right)\right]^{-1}\right\}\right)^{1/3} \tag{24}$$

Since $n_0 \gg 1$, the second term on the r.h.s. of (24) can be neglected in our considerations. Then, for all values $3kT < \rho_0\overline{\omega}$ the probability distribution function (10) for the density fluctuations in a one-phase fluid system is not longer determined. Therefore, Eq. (24) can be interpreted as one which determines a curve bounding the region in which the one-phase fluid system cannot exist. In other words. Eq. (24) describes the coexistence curve. Since the probability distribution function (10) becomes uniform when the relation $3kT = \rho_0\overline{\omega}$ is fulfilled, we can find the approximate numerical value of $\langle\delta^2\rangle$ for states on the coexistence curve without knowing the value of the parameter n_0. From Eq. (22) we obtain a value of $\frac{1}{3}$ for $\langle\delta^2\rangle$ on the coexistence curve. Substituting this value into Eq. (9) and taking into account that Eq. (24) is fulfilled at the critical point, we obtain the law of corresponding states in the form

$$P_cV_c/RT_c = 0.33 - a \tag{25}$$

The calculations of the whole isotherms involve complicated calculations of the radial distribution function $g(r)$.(15) Let us stress the fact that the limits of the integrals in Eq. (22) leading to the defined value of $\langle\delta^2\rangle$ for all states including the critical state are direct consequences of Eq. (5) and the obvious condition (21).

5. MORE PRECISE CALCULATIONS

In previous sections we assumed density independence of ω described by Eq. (4). The radial distribution function $g(r)$ in formula (4) depends in fact not only on the distance r but also on the density and temperature.(16) Therefore, we should write it as $g(r, \rho, T)$. In the case of density fluctuations it also depends on the parameter δ. That is why Eq. (24) can be treated as the first, very rough approximation of the coexistence curve. One can easily deduce that the values of pressure for a gas phase and a liquid phase are not the same on the coexistence curve given by Eq. (24) for the same temperature excluding the critical point. The lower the temperature, the worse is the approximation given by Eq. (24). This just results from the assumption that ω does not depend on ρ. Since the analytical form of the function $g(r, \rho, T)$ remains unknown, one can expand the quantity ω in a Taylor series about its equilibrium value ω_0

$$\omega(\rho) = \omega_0 + \left(\frac{\partial\omega}{\partial\rho}\right)_0\Delta\rho + \frac{1}{2}\left(\frac{\partial^2\omega}{\partial\rho^2}\right)_0\Delta\rho^2 + \cdots \tag{26}$$

where $\Delta\rho = \rho_0\delta$. The last expansion gives the correction to the Eq. (8), which takes the form

$$W = -\frac{1}{2}\rho_0\omega_0 N\left\{1 + \left[1 + \frac{2\rho_0}{\omega_0}\left(\frac{\partial\omega}{\partial\rho}\right)_0 + \frac{1}{2}\frac{\rho_0{}^2}{\omega_0}\left(\frac{\partial^2\omega}{\partial\rho^2}\right)_0\right]\langle\delta^2\rangle + \cdots\right\} + W_l$$

and consequently the formula (9) for pressure in the whole system should be also corrected as follows:

$$P = kT\rho_0 - \frac{1}{6}\rho_0{}^2\omega_0\left\{1 + \left[1 + \frac{2\rho_0}{\omega_0}\left(\frac{\partial\omega}{\partial\rho}\right)_0 + \frac{1}{2}\frac{\rho_0{}^2}{\omega_0}\left(\frac{\partial^2\omega}{\partial\rho^2}\right)_0\right]\langle\delta^2\rangle\right\} - akT\rho_0 \tag{27}$$

The last equation is expressed of course in the approximation to the terms with $\langle\delta^2\rangle$ only.

Incidentally, the expansion (26) is equivalent to the virial expansion. In other words, one can say that the third virial coefficient is proportional to the first derivative and next coefficients to successive derivatives in (26).

To calculate the mean square fluctuation more precisely, we should express ΔP in terms of the parameter δ, taking into account the expansion (26) and carrying out the integration over δ instead of v in Eq. (13). The local, isothermal change of pressure due to the density fluctuation with the parameter δ will take the form

$$\Delta P = (kT - \tfrac{1}{3}\rho_0\omega_0)\rho_0\delta - \tfrac{1}{6}\rho_0{}^2\omega_0\delta^2 - \tfrac{1}{6}\rho_0{}^2(1+\delta)^2\,\Delta\omega \tag{28}$$

where $\Delta\omega = \omega(\rho) - \omega(\rho_0)$. Substituting (28) into (13), using (26), and taking into account $dv = (dv/d\delta)\,d\delta$ and, from (11), $\partial v/\partial\delta = -v_0/(1+\delta)^2$, we obtain

$$L(\delta) = n_0\left\{\left(kT - \frac{1}{3}\rho_0\omega_0\right)\int_0^\delta \frac{\delta}{(1+\delta)^2}\,d\delta - \frac{1}{6}\rho_0\omega_0\int_0^\delta \frac{\delta^2}{(1+\delta)^2}\,d\delta - \frac{1}{6}\rho_0\sum_{l=1}^{\infty}\frac{1}{l!}\rho_0{}^l\left(\frac{\partial^{(l)}\omega}{\partial\rho^{(l)}}\right)_0\int_0^\delta \delta^l\,d\delta\right\} \tag{29}$$

Evaluating the integrals in Eq. (29), we can write the work L as a series

$$L(\delta) = n_0\sum_{l=1}^{\infty} A_l\delta^{l+1} \tag{30}$$

where

$$A_l = (-1)^{l+1}\left(\frac{l}{l+1}kT - \frac{1}{6}\rho_0\omega_0\right) - \frac{1}{6}\rho_0^{l+1}\frac{1}{l!\,(l+1)}\left(\frac{\partial^{(l)}\omega}{\partial\rho^{(l)}}\right)_0 \tag{31}$$

Applying the formulas (10), (22), (30), and (31), we obtain the following expression for the mean square fluctuation in the particle density:

$$\begin{aligned}\langle\delta^2\rangle = {} & \left(\int_{-1}^{+1} \delta^2 \exp\left\{-\frac{n_0}{kT}\sum_{l=1}^{\infty}\left[(-1)^{l+1}\left(\frac{l}{l+1}\,kT - \frac{1}{6}\,\rho_0\omega_0\right)\right.\right.\right. \\ & \left.\left.\left. - \frac{1}{6}\,\frac{1}{l!\,(l+1)}\,\rho_0^{l+1}\left(\frac{\partial^{(l)}\omega}{\partial\rho^{(l)}}\right)_0 \delta^{l+1}\right]\right\} d\delta\right) \\ & \times \left(\int_{-1}^{+1} \exp\left\{-\frac{n_0}{kT}\sum_{l=1}^{\infty}\left[(-1)^{l+1}\left(\frac{l}{l+1}\,kT - \frac{1}{6}\,\rho_0\omega_0\right)\right.\right.\right. \\ & \left.\left.\left. - \frac{1}{6}\,\frac{1}{l!\,(l+1)}\,\rho_0^{l+1}\left(\frac{\partial^{(l)}\omega}{\partial\rho^{(l)}}\right)_0 \delta^{l+1}\right]\right\} d\delta\right)^{-1} \qquad (32)\end{aligned}$$

Equation (30) can be rewritten in the form

$$L(\delta) = n_0\{[\tfrac{1}{2}kT - \tfrac{1}{6}\rho_0\omega_0(1 + \lambda(\rho_0, T))]\delta^2 + R\} \qquad (33)$$

where

$$\lambda(\rho_0, T) = \frac{1}{2}\,\frac{\rho_0}{\omega_0}\left(\frac{\partial\omega}{\partial\rho}\right)_0 \qquad (34)$$

For some particular values of T and ρ_0 the first term on the r.h.s. of Eq. (33) vanishes. This means that in these cases the work $L(\delta)$ is equal to n_0R. Analyzing Eqs. (30) and (31), one can deduce that the probability (10) becomes abnormally high for positive fluctuations [and can even be undetermined, since the exponent in (10) may be positive] and very small for negative values of δ, when the following equation is satisfied

$$3kT = \rho_0\omega_0[1 + \lambda(\rho_0, T)] \qquad (35)$$

This means that for the states described by Eq. (35) a fluid system has an abnormal tendency to create condensations which lead to the phase transitions. Thus, Eq. (35) can be interpreted as the coexistence curve. Equation (30) is determined for a representative subsystem. Since, however, the total number of atoms in a closed system is constant, it seems to be reasonable to assume that the probabilities for negative and positive fluctuations are the same and approximately equal to one with the normalizing constant equal to 1/2 on the coexistence curve. The last assumption is equivalent to the assumption that the numbers and mean volumes of negative and positive fluctuations are the same.

It has been shown in Section 4 that the general stability criterion introduced in the form (19) leads in first approximation to the vanishing of the probability index. This result is convergent with the stability criterion introduced by Smoluchowski.(4) On the other hand, Smoluchowski(5) pointed out and Einstein(17) supported the idea that higher-order terms in the thermodynamic potential are indispensible in the description of the critical state. This was also confirmed by Kociński *et al.*(18) in studies of the phenomenon of critical scattering of neutrons in ferromagnets. Incidentally, the well-known expansion in the Landau theory of phase transitions can be traced back to the original papers of Smoluchowski. Taking into consideration the higher-order terms in the thermodynamic potential leads to the nonuniform probability distribution function at the critical point. Although the coefficients (31) in series (30) do not result from the expansion of the thermodynamic potential with respect to the thermodynamic variables, the general form of the probability distribution function given by (10) and (30) is analogous with one introduced by Smoluchowski.

Equation (35), suggested as the equation of the coexistence curve, can be derived more formally. For this purpose we shall apply the general criterion of stability given in the form (19). We shall carry out our considerations in the approximation to the terms with δ^2 only. This means that only the first term in the series (30) will be taken into account.

In this approximation the mean square fluctuation will be expressed by the general formula (22) but α will now take the form

$$\alpha = kT - \tfrac{1}{3}\rho_0\omega_0 - \tfrac{1}{6}\rho_0{}^2(\partial\omega/\partial\rho)_0 \tag{36}$$

In the same approximation, from Eq. (28) we obtain the value δ_c described in Section 4,

$$\delta_c = 6\alpha/A \tag{37}$$

where

$$A = \rho_0\omega_0 + 2\rho_0{}^2\left(\frac{\partial\omega}{\partial\rho}\right)_0 + \frac{\rho_0{}^3}{2}\left(\frac{\partial^2\omega}{\partial\rho^2}\right)_0 \tag{38}$$

Substituting Eqs. (23) and (37) into (19) and taking into account (36), we obtain an equation analogous to Eq. (24),

$$kT = \frac{1}{3}\rho_0\omega_0 + \frac{1}{6}\rho_0{}^2\left(\frac{\partial\omega}{\partial\rho}\right)_0 + n_0{}^{-1/3}\left(\frac{kTA^2}{36}\left\{1 - \left[{}_1F_1\left(1; \frac{3}{2}; \frac{n_0\alpha}{2kT}\right)\right]^{-1}\right\}\right)^{1/3} \tag{39}$$

Neglecting the last term on the r.h.s. of (39) because $n_0 \gg 1$, we obtain Eq. (35) with $\lambda(\rho_0, T)$ described by (34).

For the critical point the density of the gas phase is equal to the density of the liquid phase. This leads to the demand for the same value of the parameter $\lambda(\rho_0, T)$. It results from our analysis of the dependence of the internal virial on the density that this condition can be met only by $\lambda = 0$, which corresponds to the maximal value of ω_0 at the critical point. Thus, at the critical point $3kT = \rho_0\omega_0$ and we obtain almost the same value for the critical ratio as that given by Eq. (25). The undetermined parameter a will be somewhat changed due to the correction to the equation of state given by the expansion (26). The parameter $\lambda(\rho_0, T)$ determined by Eq. (34) is positive for the part of the coexistence curve on the gas-phase side and negative on the liquid-phase side.

6. APPROXIMATIONS

The assumption of the homogeneous fluctuation model is the most crucial physical approximation made in our description of the phase transition in a fluid system. The density fluctuations are, in fact, inhomogeneous and would be described adequately in terms of the correlation function to which the spatial distribution of the particle density in fluctuation is related. Rewriting the whole theory in terms of the correlation function instead of the parameter δ is, at least in principle, possible, but it involves real mathematical difficulties. The pair distribution function $g(r)$ used in Eq. (4) is a measure of the probability of finding a pair of particles separated by a distance $\mathbf{r}$; clearly, the product $g(\mathbf{r})\, d^3\mathbf{r}$ determines the probability of finding a particle in the volume element $d^3\mathbf{r}$ around the point $\mathbf{r}$ when we already have a particle at the point $\mathbf{r} = 0$. For a homogeneous system of N particles each particle chosen as a central one is equally likely to be at any point in the space available to it, and the radial distribution function $g(r)$ depends mainly on the form of the interaction potential. In other words, the function $g(r)$ plays the role of the correlation between molecules over microscopic distances. The range of this function is of the same order as the range of the interaction potential. For a homogeneous system the function $g(r)$ can be determined by means of the proper integral equation.(15) The determination of the function $g(r)$ becomes much more complicated for an inhomogeneous system because in this case the function $g(r)$ depends also on the macroscopic spatial distribution of the particle density. In an inhomogeneous system all particles cannot be treated as equivalent to a central one since the microscopic correlation depends on the position of the particle chosen as central. On the other hand, the condensation can be regarded as a static phenomenon and should be well described in terms of the mean square fluctuation. It can be assumed that the mean square fluctuation calculated for a homogeneous fluctuation does not differ too much in comparison with one calculated for an inhomogeneous fluctuation.

We have assumed that the fluctuations in density and temperature are statistically independent. It must be pointed out that this is also the approximation. Such independence can be proved only to second-order terms in the expansion of the thermodynamic potential. In an exact approach the connection between fluctuations in temperature and density must be taken into account. The last remark is connected with the theory of fluctuations. We have applied the well-known statements of the theory formulated for small fluctuations. As far as the theory is undoubtedly correct for small fluctuations, the extrapolation of the theory to the case of large fluctuations in the vicinity of the critical state may be questioned. On the other hand, the theory of fluctuations is not developed sufficiently in general and a better theory which could be applied for a description of fluctuations in the critical state is not known.

7. CONCLUSIONS

Our aim has been to show that the density fluctuations must be taken into consideration in the derivation of the equation of state. Fluctuations in the particle density cannot be neglected, particularly in the vicinity of the phase transition since they give significant corrections to the equation of state. Without using any experimental parameter the fluctuation theory gives better agreement with experimental results than other theories. The value P_cV_c/RT_c obtained from Eq. (9) is compared with other theoretical results and an average experimental value for several gases in Table I.

It results from Eq. (9) or (27) and (22) that the increase of $\langle\delta^2\rangle$ with compression of a gas or expansion of a liquid flattens the isotherms in the critical region.

The density fluctuations are responsible not only for the phenomenon of critical opalescence but also for the phase transition in a fluid system. The coexistence curve [Eq. (24), (35), or (39)] has been obtained analytically. Unphysical parts of the van der Waals isotherms in fact never appear in the theory. It is worthwhile to mention that the Eq. (9) or (27) has a physical sense only for a one-phase system. We do not discuss in this paper the horizontal part of an isotherm which describes the coexistence of a gas and a liquid.

Table I

	P_cV_c/RT_c
Mean value for Ne, N_2, Ar, CH_4	0.292
From Eq. (9)	0.33
Lennard–Jones and Devonshire$^{(19)}$	0.591
Van der Waals	0.375
Cernushi and Eyring$^{(20)}$	0.342
Peek and Hill$^{(21)}$	0.719
Ono$^{(22)}$	0.342
Mayer and Careri$^{(23)}$	0.676

The full discussion of the two-phase region can be found in the paper by van Kampen.(24) Our theory gives the phase transition analytically for a finite fluid system without recourse to the thermodynamic limit and explains the mechanism of condensation.

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