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# Fluctuation Theory of Critical Phenomena in Fluids

**G. A. Martynov**

*Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, 117071 Russia*
*e-mail: g2302@migmail.ru*

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**Abstract**—It is assumed that critical phenomena are generated by density wave fluctuations carrying a certain kinetic energy. It is noted that all coupling equations for critical indices are obtained within the context of this hypothesis. Critical indices are evaluated for 15 liquids more accurately than when using the current theory of critical phenomena.

*Keywords:* critical phenomena, kinetic energy, critical indices

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## INTRODUCTION

The modern theory of critical phenomena (the scaling theory) is based on the concept of universal similarity, according which critical indices must be uniform for all substances with the same symmetry [1]. Since all liquids and gases belong to the same class of symmetry, their indices must be uniform. Experiments initially seemed to confirm this hypothesis. With the increased accuracy of measurements, however, data indicating a discrepancy between theory and experiment emerged. Tables 1 and 2[1] contain the results from measuring the critical indices for 15 liquids, obtained by at least 35 authors. It follows from these data that the indices of different liquids always vary; moreover, they never agree with the predictions of scaling theory. The discrepancies between the theory and experiment are slight; as a rule, they do not exceed 10%. However, their magnitudes are always greater than the uncertainty of measurement. Of course, we may assume that the observed discrepancies are due to measurements being made too far from the critical point. In the literature, however, there are two especially precise results obtained by measuring the critical indices for $SF_6$ and $CO_2$ [3, 4]. The researchers managed to approach the immediate critical region over a distance on the order of $10^{-5}$ K. The result was critical index β, equal to 0.35 at $\tau = \dfrac{\theta - \theta_c}{\theta_c} > 3\times10^{-4}$, beginning to steadily approach its classical value $\beta = 0.5$ at $\tau < 3\times10^{-4}$ instead of approaching scaling value $\beta = 0.3245$ (here, $\theta = k_BT$ is temperature). The other indices all started to approach their classical values as well. This behavior was later confirmed by a German research group in [3, 4].

Following an unwritten law of physics, if there is a discrepancy between theory and experiment, theory is to blame. In this particular case, however, the view that the experiment was the cause of the problem prevailed, since the gravitational effect was not properly considered. Gravitation can indeed affect the magnitudes of critical indices, but it has been impossible to prove that it would eliminate the observed discrepancy despite twenty years of efforts by several hundred authors [5].

The data in Tables 1 and 2 indicate that the critical indices of different indices vary. This discrepancy is, of course, very small. However, it is sufficient to assume that the critical indices are not absolute, and the concept is far from universality.[2] What, then, is the explanation is for the dependence of critical indices on the nature of a substance? The aim of this work is to answer to this question.

## CRITICAL PHENOMENA AND FLUCTUATIONS

As is well known, critical point coordinates $\rho_c, \theta_c$ on the phase diagram are determined by the equations

$$\frac{1}{\theta}\frac{\partial P(\rho_c,\theta_c)}{\partial \rho} = 0, \quad \frac{1}{\theta}\frac{\partial^2 P(\rho_c,\theta_c)}{\partial \rho^2} = 0, \tag{1}$$

where pressure $P$, which in statistical mechanics is determined using Bogolyubov's equation

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[1] The data presented in Tables 1 and 2 were taken from [2].

[2] In *The Modern Theory of Critical Phenomena*, Ma Shang-keng referred to the concept of universality as "artless and primitive" [6].

**Table 1.** Values of $\Delta\beta = \beta_{\exp} - 0.333$

| Substance | $^3He$ | $^4He$ | Ar | Xe |
|---|---|---|---|---|
| $\Delta\beta$ | $0.028 \pm 0.0005$ | $0.028 \pm 0.003$<br>$0.006 \pm 0.006$ | $0.007 \pm 0.001$<br>$0.007 \pm 0.002$ | $-0.016 \pm 0.004$<br>$-0.004$<br>$0.004 \pm 0.003$ |
| Substance | $N_2$ | $O_2$ | $CO_2$ | $SF_6$ |
| $\Delta\beta$ | $0.025 \pm 0.001$ | $0.020 \pm 0.005$ | $-0.012$<br>$-0.009 \pm 0.009$<br>$0.014, 0.014$ | $-0.006 \pm 0.005$ |
| Substance | $CH_4$ | $C_5H_{12}$ | $C_6H_6$ | $C_6H_{14}$ |
| $\Delta\beta$ | $0.024$ | $0.02 \pm 0.02$ | $0.02 \pm 0.02$ | $0.0032 \pm 0.014$ |
| Substance | $C_7H_{16}$ | $CHF_3$ | $CF_3Cl$ | $H_2O$ |
| $\Delta\beta$ | $0.007 \pm 0.04$<br>$0.025 \pm 0.009$<br>$0.052 \pm 0.016$ | $0.000$ | 000 | $0.013$ |

The values of $\beta$ were taken from Table 2.

$$\frac{1}{\theta}P = \rho - \frac{1}{6}\rho^2 \int_0^\infty r\frac{\partial[\Phi(r)/\theta]}{\partial r}G(r;\rho,\theta)\,4\pi r^2 dr, \qquad (2)$$

is derived from the canonical distribution (CD) function via identity transformations (in (2), $\rho = N/V$ is the density of particles, $\Phi(r)$ is the potential of interaction, and $G(r;\rho,\theta)$ is the two-particle distribution function).

By expanding $G(r;\rho,\theta)$ into a series according to powers of density, we obtain the common virial series $\theta^{-1}P(\rho,\theta) = \sum_{k=1}^{\infty}\rho^k B_k(\theta)$. Moving to variable $\Delta\rho = \rho - \rho_c$ and assuming that $\theta = \theta_c$, we transform it into the series $P(\rho,\theta_c) = P_c + b_3(\theta_c)\Delta\rho^3 + b_4(\theta_c)\Delta\rho^4 + \ldots$ in terms of powers of $\Delta\rho$, where the coefficients are $b_1 = b_2 = 0$ because of conditions (1). It follows that $P \to P_c + b_3\Delta\rho^3$ for $\Delta\rho \to 0$. Within the standard approximation, and assuming that the CD function at low densities can be expanded into a power series of density, we can thus establish that critical index $\delta$ must always be equal to 3 (or possibly 4, if $b_3 = 0$). At the same time, experiments reliably show that $\delta = 4.3$–$4.7$. Such noncoincidence indicate that describing critical phenomena is beyond the capabilities of the standard theory of equilibrium systems based on the CD function.

As is well known, there are always fluctuations of density and temperature in any equilibrium systems. Strictly speaking, equilibrium systems are therefore nonequilibrium. However, the amplitude of fluctuations is negligibly small, so the contribution from fluctuations is systematically ignored. As we approach the critical point, however, the amplitude gradually grows to infinity at the critical point. We may therefore assume that the special properties of substances in the vicinity of critical point are determined by these fluctuations. It should be noted that fluctuations are nonequilibrium phenomena: they arise at one moment and disappear at the next; in addition, they appear in unpredictable point $\mathbf{r}$ and at unpredictable moment of time $t$. A consistent description of them is possible only in terms of the theory of *non-equilibrium* phenomena (see, e.g., [7, 8]). However, the theory of *equilibrium* systems has been always based on the assumption that all parameters of substance are time-invariant and uniform over an entire system. How can we combine the nonequilibrium origin of fluctuations with the thermodynamically equilibrium state of an entire system?

## THE CANONICAL DISTRIBUTION FUNCTION AND FLUCTUATIONS

In statistical mechanics, the state of a closed isolated system of $N$ particles that occupies a volume $V$ is described by $N$ particle distribution function $G_{(N)}$, regardless of whether or not the system is in equilibrium [8]. In the general case, this function depends on coordinates $\mathbf{r}$ and pulses $\mathbf{p}_i$ of all particles, and on density $\rho(\mathbf{r},t)$ and temperature $\theta(\mathbf{r},t)$, which characterize the macroscopic state of the system at given point $\mathbf{r}$ and given moment $t$. Condition $\rho, \theta = \mathrm{const}$ is commonly assumed in the theory of equilibrium systems. Nevertheless, fluctuations are present in any equilibrium system. It is therefore always true that

**Table 2.** Critical indices of different liquids

| Substance | $\alpha$ | $\beta$ | $\gamma$ | $\delta$ | $\eta$ |
|---|---|---|---|---|---|
| Scaling theory | 0.1120 | 0.3245 | 1.239 | 4.82 | 0.0312 |
| Fluctuation hypothesis | 0.11 | 0.3333 | 1.224 | 4.673 | 0.058 |
| $^3$He | 0.105 | 0.361 ± 0.005 | – | – | – |
| | 0.11 | 0.361 | 1.156 | 4.202 | 0.153 |
| $^4$He | 0.115 ± 0.006;<br>0.108 ± 0.010 | 0.3554 ± 0.0028;<br>0.339 ± 0.006 | 1.20 ± 0.02;<br>1.223 ± 0.017 | – | |
| | 0.110 | 0.339 | 1.21 | 4.57 | 0.076 |
| Ar | 0.117 ± 0.001;<br>0.11 ± 0.02 | 0.340 ± 0.001;<br>0.340 ± 0.002 | – | 4.49 | |
| | 0.110 | 0.340 | 1.21 | 4.53 | 0.085 |
| Xe | 0.11; 0.08 | 0.317 ± 0.004;<br>0.329;<br>0.337 ± 0.003 | 1.23 | 4.74 | 0.045 |
| | 0.110 | 0.333 | 1.22 | 4.67 | 0.058 |
| $N_2$ | 0.11 ± 0.03 | 0.358 ± 0.001 | 1.19 | 4.28 | 0.13 |
| | 0.11 | 0.352 | 1.19 | 4.37 | 0.12 |
| $O_2$ | – | 0.353 ± 0.005 | – | – | – |
| | 0.110 | 0.353 | 1.18 | 4.35 | 0.117 |
| $CO_2$ | 0.10; 0.125 ± 0.02 | 0.321; 0.324 ± 0.009; 0.347; 0.347 | 1.226 ± 0.007 | 4.30 ± 0.1;<br>4.576; 4.851 | 0.077 |
| | 0.10 | 0.347 | 1.21 | 4.52 | 0.08 |
| $SF_6$ | 0.08 | 0.327 ± 0.005;<br>0.339 ± 0.002; | 1.16; 1.22 ± 0.06;<br>1.28; | 4.99(?) | – |
| | 0.11 | 0.333; | 1.22; | 4.67 | 0.06 |
| $CH_4$ | 0.11; 0.057 | 0.357 | 1.230 | 4.450 | 0.101 |
| | 0.09 | 0.357 | 1.186 | 4.51 | 0.09 |
| $C_5H_{12}$ | – | 0.35 ± 0.02 | 1.25 ± 0.10 | 5.0 ± 0.5 | – |
| | 0.110 | 0.350 | 1.19 | 4.40 | 0.11 |
| $C_6H_6$ | – | 0.35 ± 0.02 | 1.30 ± 0.05 | – | – |
| | 0.110 | 0.350 | 1.19 | 4.40 | 0.11 |
| $C_6H_{14}$ | – | 0.365 ± 0.014 | 1.14 | – | – |
| | 0.110 | 0.365 | 1.16 | 4.18 | 0.16 |
| $C_7H_{16}$ | – | 0.340 ± 0.04;<br>0.358 ± 0.009;<br>0.385 ± 0.016; | – | – | – |
| | 0.11 | 0.358 | 1.17 | 4.28 | 0.14 |
| $CHF_3$ | – | 0.333 | | | |
| | 0.110 | 0.333 | 0.12 | 4.67 | 0.058 |
| $CF_3Cl$ | – | 0.333 | | | |
| | 0.11 | 0.333 | 0.12 | 4.67 | 0.058 |
| $H_2O$ [14] | 0.11 | 0.346 | 1.20 | 4.50 | |
| | 0.110 | 0.346 | | 4.46 | 0.098 |

The experimental data obtained by different authors were taken from Table 2.6 in [2]. These data are in the upper line of the table for each substance; below them are data calculated using the coupling equations for the values of indices of $\alpha$ and $\beta$ indicated in two first rows of Table 2.

$$\rho(\mathbf{r},t) = \rho_0 + \delta\rho(\mathbf{r},t), \quad \theta(\mathbf{r},t) = \theta_0 + \delta\theta(\mathbf{r},t) \tag{3}$$

and so

$$\begin{gathered} G_{(N)}(\rho_0 + \delta\rho, \theta_0 + \delta\theta) = G^{(0)}_{(N)}(\rho_0, \theta_0) \\ + \frac{\partial G^{(0)}_{(N)}}{\partial\rho}\delta\rho(\mathbf{r},t) + \frac{\partial G^{(0)}_{(N)}}{\partial\theta}\delta\theta(\mathbf{r},t) + \dots, \end{gathered} \tag{4}$$

where $\delta\rho$ and $\delta\theta$ are the fluctuations of density and temperature that meet the condition $\overline{\delta\rho} = 0$, $\overline{\delta\theta} = 0$. If we confine ourselves in Eq. (4) to quadratic terms of the series and average the obtained expression over all values of $\mathbf{r}$ and $t$, we obtain

$$\begin{gathered} G_{(N)}\left[r_{ij};\, \rho(\mathbf{r},t), \theta(\mathbf{r},t)\right] = G_{(N)}\left(r_{ij}, \mathbf{p}_i;\, \rho_0, \theta_0\right) \\ + \frac{1}{2}\left[\frac{\partial^2 G_{(N)}\left(r_{ij}, \mathbf{p}_i; \rho_0, \theta_0\right)}{\partial\rho^2}\overline{\delta\rho^2} \right. \\ \left. + \frac{\partial^2 G_{(N)}\left(r_{ij}, \mathbf{p}_i; \rho_0, \theta_0\right)}{\partial\theta^2}\overline{\delta\theta^2}\right]. \end{gathered} \tag{5}$$

In this expression, the additional term enclosed in square brackets is always positive. Hence, the energy of the entire system is

$$\begin{gathered} E_{(N)} = \int_\Gamma H_{(N)}(\mathbf{r}_{ij}, \mathbf{p}_i) G_{(N)} \\ \times \left(\mathbf{r}_{ij}, \mathbf{p}_i;\, \rho_0 + \delta\rho, \theta_0 + \delta\theta\right) dX_{(N)} \\ = E^{(0)}_{(N)}(\rho_0, \theta_0) + N\theta\phi(\rho_0, \theta_0) > E^{(0)}_{(N)}, \end{gathered} \tag{6}$$

where $E^{(0)}_{(N)} = Ne(\rho_0, \theta_0)$; $e = \frac{3}{2}\theta_0 + \frac{1}{2}\rho_0\int_0^\infty \Phi(r) G(r; \rho_0, \theta_0) 4\pi r^2 dr$ is the standard expression for energy obtained in the approximation $\rho(\mathbf{r},t) = \rho_0$, $\theta(\mathbf{r},t) = \theta_0$; while $\delta E_{(N)} = N\theta\phi(\rho_0, \theta_0)$ is the contribution from fluctuations to Eq. (6), $G(r; \rho_0, \theta_0)$ is the two-particle distribution function, and $dX_{(N)} = \frac{d\mathbf{r}_1 \dots d\mathbf{r}_N}{V^N}\frac{d\mathbf{p}_1 \dots d\mathbf{p}_N}{P^{3N}}$). Since pressure $P$ is associated with energy $E_{(N)}$ by the familiar thermodynamics formula $\frac{\partial E}{\partial V} = \theta\frac{\partial P}{\partial\theta} - P$, we find that

$$P = P^{(0)} + \delta P = P^{(0)} + \rho^2\theta\frac{\partial\phi}{\partial\rho}, \tag{7}$$

where $P^{(0)}$ is the pressure calculated in approximation $\rho, \theta = \text{const}$ (see Eq. (2)).

The same formulas can be obtained in another way. It is generally believed that the potential energy of a system is $U_{(N)} = \sum_{i,j=1}^N \Phi(r_{ij})$, where potential $\Phi(r) \to 0$ when $r \to \infty$. Due to fluctuations, however, widely spaced particles have energy equal to $\theta\phi$, not zero. This is why we assume that $\Phi_{\text{eff}} = \Phi(r) + \theta\phi$. Such renormalization does not change the initial Hamilton equations that form the basis of statistical mechanics, since $\phi$ is invariant with the coordinate of particles and therefore disappears from all equations after differentiation with respect to $\mathbf{r}$ and $\mathbf{p}$. At the same time, the emergence of an additional term changes the distribution of particles within the correlation sphere, since the effective density and effective temperature in the correlation sphere are different from the seed values obtained in the approximation of $\rho_0, \theta_0$.

After substituting initial potential $\Phi$ for effective potential $\Phi + \theta\phi$, the CD function becomes

$$G_{(N)} = \frac{e^{-N\phi}}{Q_{(N)}}\exp\left(-\sum_{i,j=1}^N \Phi_{ij}/\theta\right),$$

$$\begin{gathered} Q_{(N)} = e^{-N\phi}\frac{1}{V^N}\int_V \exp\left(-\sum_{i,j=1}^N \Phi_{ij}/\theta\right) d\mathbf{r}_1 \dots d\mathbf{r}_N \\ = e^{-N\phi} Q^{(0)}_{(N)}. \end{gathered}$$

Hence, the free energy of the system is

$$F_{(N)} = -\theta \ln Q_{(N)} = F^{(0)}_{(N)} - N\theta\phi. \tag{8}$$

Using standard thermodynamics formulas, it is now easy to show that

$$\begin{gathered} e = \theta\left(\frac{3}{2} + \phi\right) + \frac{1}{2}\rho\int_0^\infty \Phi(4) G^{(0)}_{(2)} 4\pi r^2 dr, \\ P = \rho\theta\left(1 + \rho\frac{\partial\phi}{\partial\rho}\right) \\ - \frac{1}{6}\rho^2\int_0^\infty r\frac{\partial\Phi(r)}{\partial r} G_{(2)}(r; \rho, \theta) 4\pi r^2 dr. \end{gathered} \tag{9}$$

These equations correspond to the above relationships. Equation (5) thus allows us to limit the contribution from fluctuations to the thermodynamic parameters merely to the emergence of additional terms in all thermodynamics equations that include the kinetic energy of fluctuations. This was to be expected, since the theory is structured in additive approximations, according to Eqs. (3)–(5). However, the contribution from fluctuations generally takes a more sophisticated form.

## POTENTIAL COMPONENT OF CRITICAL PHENOMENA

All thermodynamic parameters of a substance generally have two components: potential and fluctuation. Let us first consider the behavior of the potential component.

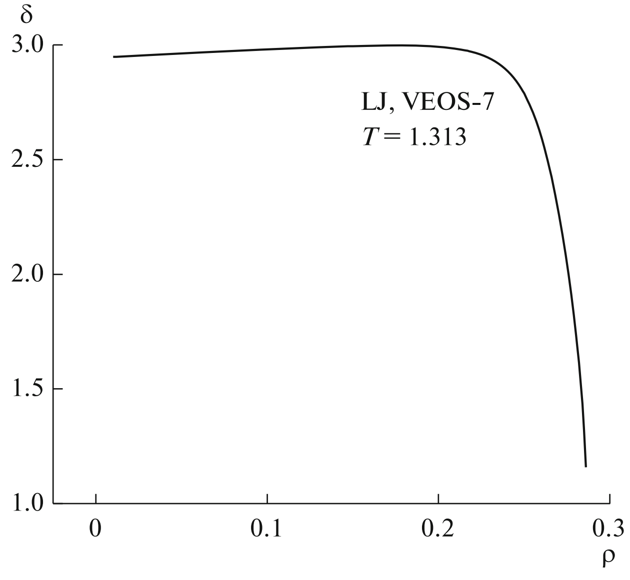

**Fig. 1.** Dependences of index $\delta(\rho)$ in formula $\delta P = (P - P_0)/P_0 = \zeta^{\delta(\rho)}$ for an LJ liquid at the critical isotherm.

Pressure $P^{(0)}(\rho, \theta)$ at low densities can be always written as virial series $P^{(0)} = \sum_{k=1}^{\infty} \rho^k B_k(\theta)$. The first seven coefficients $B_k(\theta)$ of this series have so far been computed for the Lennard-Jones (LJ) potential using a canonical distribution function that allows us to estimate pressure at densities $\rho \le \rho_c$ with an error no greater than 0.01%. Using the obtained seven-term polynomial and conditions (1) for the coordinates of the critical point, critical density $\rho_c = 0.287$, critical temperature $\theta_c = 1.313$, and critical pressure $P_c = 0.128$ were calculated for an LJ liquid in [9].

To use the resulting polynomial to describe critical phenomena, it must be written in the standard form accepted in the theory of critical phenomena,[3]

$$\delta P(\xi) = \frac{P(\xi, \tau) - P_c}{P_c} = \xi^{\delta}, \tag{10}$$

where in the general case,

$$\delta = \delta(\xi, \tau), \quad \xi = \frac{\rho - \rho_c}{\rho_c}, \quad \tau = \frac{\theta - \theta_c}{\theta}.$$

Here, $\delta(\xi, \tau)$ is the critical index; it is generally fractional, since expansion is preformed around the singular point. Changes in the sign of $\xi$ in this case convert the real function into a complex one, indicating singularity at this point for the statistical sum.

Using the virial series to determine the form of function $\delta P(\xi, 0)$ on the critical isotherm, index $\delta = \delta(\xi, 0)$ can be calculated using Eq. (10). Figure 1 shows the dependence of this function at critical temperature $\theta_c$. We can see that the dependence of $\delta P$ on density $\xi$ is accurately described by formula $\delta P = \xi^3$ with index $\delta(\xi, 0) = 3 = \text{const}$. After the intersection of the crossover, however, power exponent $\delta(\xi, 0)$ tends to zero instead of growing according to law $\delta P = \xi^{4.818}$, as is predicted by the scaling theory. As a result, the potential component of the pressure becomes nearly constant and equal to $P_c$ within the crossover (this equation is valid only at the critical point). This is confirmed by the data of molecular dynamics, according to which pressure is virtually constant within the $0.285 < \rho < 0.350$ range of densities (i.e., within the crossover) [10]. Derivative $\partial P/\partial \rho$ is very low throughout this range (it is strictly equal to zero at the critical point). Hence, the variations in the potential component of pressure are also insignificant throughout the critical range. At the same time, the variations in pressure in the regular part of phase diagram follow the law $\delta P \approx \xi^3$; i.e., they occur quite rapidly on the same critical isotherm. It is obvious that the point of the transition from the regular to the critical mode determines the position of the crossover separating the critical and regular regions. This finding, based on an examination of the virial series, is in direct contradiction with the generally accepted view that the position of crossover is determined by the condition for the disappearance of the pressure's fluctuation component [11].

## IVANOV EFFECT

Let us consider the behavior of the complete pressure on the critical isotherm. According to [9], it must be equal to a sum of two components within the crossover:

$$P = b_3 \Delta\rho^3 + \Delta\rho^{\delta}, \tag{11}$$

where, as experiments show, $\delta = 4.3\text{–}4.7$ (Table 2). To interpret experimental data using this formula, we must assume that relatively far from the critical point, potential component $P^{(0)} = b_3 \Delta\rho^3$ is much smaller than fluctuation component $\Delta\rho^{\delta}$; i.e., $b_3 \Delta\rho^3 \ll \Delta\rho^{\delta}$. This is the only instance where the state of a substance is determined by fluctuation component $\delta P = \Delta\rho^{\delta}$. As we approach the critical point, however, $\delta P \approx \Delta\rho^{4.5}$ is reduced faster than $P^{(0)} \ll \Delta\rho^3$, since the potential component is proportional to lower

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[3] We usually write $\delta P(\xi) = \Gamma(\xi) \cdot \xi^{\delta(\xi)}$. However, this means we simultaneously approximate one function, $\delta P(\xi)$, with two functions, $\delta(\xi)$ and $\Gamma(\xi)$. At the same time, there is no indication of how to determine each of them separately. Using the resulting randomness, we can always assume $\delta(\xi) = 4.818 + f(\xi)$; in a first approximation, this would have the value predicted by the scaling theory. However, this reasoning is not valid: it is typical of forcing the data to match the desired result. We therefore assume below that $\Gamma \equiv 1$.

power of $\delta$. As a result, the pressure must become classical in the vicinity of the critical point:

$$P \to b_3\Delta\rho^3 \quad \text{when} \quad \Delta\rho \to 0.$$

Ivanov was the first to observe this effect for $SF_6$ [12]. He found that when $\Delta\rho < 3\times10^{-5}\rho_c$, index $\delta$ starts to fall from fluctuation value $\delta = 4.3$ and rapidly reaches classical value $\delta = 3$. All other indices also tend toward their classical values.

The Ivanov effect is easily explained in terms of physics. It is known that in liquids and gases, waves of compression and expansion travel at the speed of sound [13]. The speed of sound falls progressively in the vicinity of the critical point, automatically slowing the velocity of fluctuation displacement throughout the volume of the system and thus reducing their kinetic energy, $\phi(\Delta\rho,\Delta\theta)$. The speed of sound falls to zero at the critical point, along with the kinetic energy of fluctuations, $\phi(0,0) = 0$. At the critical point, however, the mean distance between particles differs slightly from the one observed in the regular part of the phase diagram. Hence, the potential energy of particles at and in the immediate vicinity of the critical point is virtually the same as in the regular part of phase diagram. The critical indices must correspondingly be the same, i.e., classical, as Ivanov and his German coworkers discovered.

## ORNSTEIN–ZERNIKE EQUATION

Let us recall that in the presence of fluctuations, effective density

$$\rho_{\text{eff}} = \sqrt{\overline{\rho^2(\mathbf{r},t)}} = \sqrt{\rho_0^2 + \overline{\delta\rho^2}} \approx \rho_0 + \frac{1}{2}\frac{\overline{\delta\rho^2}}{\rho_0}$$

and effective temperature $\theta_{\text{eff}} \approx \theta_0 + \frac{1}{2}\frac{\overline{\delta\theta^2}}{\theta_0}$ differ from seed values $\rho_0, \theta_0$, and this affects the values of thermodynamic parameters. To consider these variations, we must apply the Ornstein–Zernike equation (OZ)

$$h(r_{12}) = C(r_{12}) + \rho\int_V h(r_{13})C(r_{32})d\mathbf{r}_3, \tag{12}$$

which is, as is well known, the CD function written in the form of an integral equation [8, 14]. In Eq. (12), $h(r) = G(r) - 1$ is the general correlation function, $G(r)$ is the two-particle distribution function, and $C(r)$ is the direct correlation function.

Let us first recall the main relations that follow from the OZ equation, which is written in Fourier form as

$$1 + \rho\hat{h}(k) = \frac{1}{1 - \rho\hat{C}(k)}, \tag{13}$$

where

$$\hat{h}(k) = 4\pi\int_0^\infty h(r)\frac{\sin(kr)}{kr}r^2dr,$$
$$\hat{C}(k) = 4\pi\int_0^\infty C(r)\frac{\sin(kr)}{kr}r^2dr. \tag{14}$$

When $k = 0$, the left part of Eq. (13) becomes equal to isothermal compressibility [8, 14]

$$\kappa_\theta \equiv \frac{\theta}{\partial P/\partial\rho} = 1 + 4\pi\rho\int_0^\infty h(r)r^2dr = 1 + 4\pi\rho h_2, \tag{15}$$

while the right part is transformed into the definition of the pressure derivative,

$$\frac{1}{\theta}\frac{\partial P}{\partial\rho} = \frac{1}{\kappa_\theta} = 1 - 4\pi\rho C_2. \tag{16}$$

The moments are determined as

$$C_{2k}(\rho,\theta) = \int_0^\infty C(r;\rho,\theta)r^{2k}dr,$$
$$h_{2k}(\rho,\theta) = \int_0^\infty h(r;\rho,\theta)r^{2k}dr. \tag{17}$$

The moments of function $h(r)$ are determined in the same way.

Direct correlation function $C(r;\rho,\theta)$ is an infinite series in powers of densities whose coefficients are determined by multidimensional integrals of different products of Mayer functions $f_{ij} = \exp(-\Phi_{ij}/\theta) - 1$. Thus, $C_2(\rho,\theta)$ determines only the potential component of pressure; the fluctuation component is ignored. To bring Eq. (16) into line with Eq. (9) for pressure, we need

$$\frac{1}{\theta}\frac{\partial P}{\partial\rho} = \frac{1}{\kappa_\theta} = 1 - 4\pi\rho C_2^{(0)} + 4\pi\rho\delta C_2,$$
$$\delta C_2 = \frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial\phi}{\partial\rho}\right). \tag{18}$$

As a result, direct correlation function $C(r)$ under integral (18) is equal to

$$C(r) = C^{(0)}(r) - \delta C(r), \quad \hat{C}(k) = \hat{C}^{(0)}(k) - \delta\hat{C}(k). \tag{19}$$

The moments of function $\delta C(r;\rho,\theta)$ are correspondingly written as

$$\delta C_{2k}(\rho,\theta) = \int_0^\infty \delta C(r;\rho,\theta)r^{2k}dr. \tag{20}$$

It must be emphasized that introducing additional function $\delta C(r)$, which describes the contribution from fluctuations, does not affect the potential component of direct correlation function $C^{(0)}(r)$; this is in complete agreement with the assumed additivity of the contributions from both components (see Eq. (4)).

## ASYMPTOTIC ORNSTEIN–ZERNIKE EQUATION

It is known that direct correlation function $C^{(0)}(r)$ rapidly vanishes as distance $r$ grows [14]. We assume that $R_c$ is a conditional radius beyond which $C^{(0)}(r)$ can be considered zero. For $\delta C(r)$ to have no effect on the seed state of the correlation sphere determined by function $C^{(0)}(r)$, its contribution must be concentrated at distances $r > R_c$. These distances are described by an asymptotic of the OZ equation. This is most easily studied in the space of wave vectors $k$, since values $k \to 0$ correspond to $r \to \infty$. By expanding the kernel of the Fourier transformation $\sin(kr)/kr = 1 - k^2r^2/6 + \ldots$ into a series of powers of $k$, we obtain[4]

$$\hat{C}(k) = 4\pi\left[C_2 - k^2\frac{1}{6}C_4 + \ldots\right]. \tag{21}$$

In this approximation, the OZ equation (13) becomes[5]

$$1 + \rho\hat{h}(k) = \frac{1}{(1 - 4\pi\rho C_2) + k^2 4\pi\rho C_4/6} \tag{22}$$

or, which is virtually the same thing,

$$1 + \rho\hat{h}(k) = \frac{6}{4\pi\rho C_4}\frac{1}{\lambda^2 + k^2} = \frac{1}{4\pi\rho}\frac{A}{\lambda^2 + k^2}, \tag{23}$$

where

$$\lambda(\rho,\theta) = \sqrt{6\frac{1 - 4\pi\rho C_2}{4\pi\rho C_4}}, \quad A(\rho,\theta) = \frac{6}{C_4}. \tag{24}$$

Performing inverse Fourier transformation

$$h(r) = \frac{1}{2\pi^2}\int_0^\infty \hat{h}(k)\frac{\sin(kr)}{kr}k^2dk, \tag{25}$$

we obtain

$$h(r) = \frac{A}{(4\pi\rho)^2}\frac{e^{-\lambda r}}{r}. \tag{26}$$

This formula is invariant with a particular type of direct correlation function. Therefore, substituting $C = C^{(0)}$ for $C(r) = C^{(0)}(r) - \delta C(r)$ prevents the form of solution (26) from changing. However, substituting Eq. (22) for the more complicated equation

$$1 + \rho\delta\hat{h}(k) = \frac{1}{\left[(1 - 4\pi\rho C_2^{(0)}) + 4\pi\rho\delta C_2\right] + \frac{1}{6}k^2 4\pi\rho(C_4^{(0)} - \delta C_4)}, \tag{27}$$

changes the values of both damping decrement $\lambda$ and amplitude $A$, which in this case are equal to

$$\lambda = \sqrt{6\frac{(1 - 4\pi\rho C_2^{(0)}) + 4\pi\rho\delta C_2}{4\pi\rho\left(C_4^{(0)} - \delta C_4\right)}}, \quad A = \frac{6}{4\pi\rho\left(C_4^{(0)} - \delta C_4\right)}. \tag{28}$$

## DIRECT CORRELATION FUNCTION

To move forward, we must determine the particular form of function $\delta C(r)$. It should be noted at once that it is almost impossible to find the exact form by examining the properties of equilibrium systems, since this component is generated by nonequilibrium fluctuations. Neither Hamiltonian equations nor the canonical distribution function cannot help specify $\phi$, since they have no evidence on the form of this function. Nevertheless, some features of the direct correlation function can be determined on the basis of simple and clear concepts.[6]

We have seen that in the immediate vicinity of critical point, everything is determined by a potential component with well-known properties. Below, we therefore focus on the vicinity of critical point, where the fluctuation component predominates. We can in this case ignore all potential terms in Eq. (27), simplifying the equation to

$$1 + \rho\delta\hat{h}(k) = \frac{1}{4\pi\rho\delta C_2 + k^2 2\pi\rho\delta C_2/3}. \tag{29}$$

We should note that since the additive approximation is used, only fluctuations with wavelength $\Lambda \approx 1/k \to \infty$ are considered. The contribution from the term proportional to $k^2$ is also small in this area (but it is, of course, nonzero), so we can also ignore it. In this approximation, Eq. (29) is reduces to the simple formula

$$1 + 4\pi\rho\delta h_2 = \frac{1}{4\pi\rho\delta C_2}, \tag{30}$$

where

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[4] The kernel of Fourier transformation $\sin(kr)/kr$ is determined by space dimensions $D = 3$ and is invariant with the nature of substance (i.e., function $C(r)$). This is one reason for the universality of the expressions given below.

[5] Unity in the left part of the OZ equation can be omitted, since it describes the contribution from an ideal gas [15].

[6] The use of different approximations and models (e.g, the drop model) is unavoidable in the theory of critical phenomena. The scaling theory also includes similar approximations, as Domb, one of the theory's authors, emphasized: "The renormalization group (RG) does not produce an exact solution of the Onsager type, and its application involves quite drastic approximations" ([1, p. 261]). The problem is not whether these approximations are necessary, but how they are substantiated and how well they describe experimental data.

$$\delta h_2 = \int_0^\infty \frac{A}{4\pi\rho}\frac{e^{-\lambda r}}{r}r^2 dr = \frac{A}{4\pi\rho\lambda^2}. \tag{31}$$

We first examine the left part of Eq. (30). As we approaches the critical point, experiments show that the amplitude of fluctuations rises continuously, and it is visible to the naked eye (liquids begin to opalesce more and more brightly). This dependence indicates that the amplitude of fluctuation depends on the distance to the critical point. In order to consider this effect, we must assume that $A = A(\rho, \theta; \lambda)$, where $\lambda \to 0$ as we approach the critical point. In the first approximation, we may therefore assume that

$$A(\rho, \theta; \lambda) = a(\rho, \theta)\lambda^\eta \tag{32}$$

(since expansion is performed around the singular point of the statistical sum, index $\eta$ can be nonintegral). It follows from Eq. (32) that general correlation function $\delta h(r) = \dfrac{a\lambda^\eta}{(4\pi\rho)^2}\dfrac{e^{-\lambda r}}{r}$ vanishes at the critical point where $\lambda = 0$. At the same time, however, isothermal compressibility

$$\delta\kappa_\theta(0) = 1 + 4\pi\rho_c\delta h_2 = \frac{a\lambda^\eta}{4\pi\rho_c\lambda^2} = \frac{a(\rho_c, \theta_c)}{4\pi\rho_c\lambda^{2-\eta}} \tag{33}$$

tends to infinity at the critical point.

Let us consider the right part of Eq. (30). This equation establishes the interrelation between $\delta C(r)$ and $\delta h(r)$ by definition. We therefore assume that $\delta C(r) = \delta C\left(\delta h(r)\right)$, which is necessarily a hypothesis. As noted above, however, the application of this hypothesis to the theory of critical phenomena is unavoidable.

We thus assume that $\delta C(r) = \delta C\left(\delta h(r)\right)$. Since parameter $\delta h(r)$ describes the asymptotic of the general correlation function, it must tend to zero when $r \to \infty$, in accordance with the condition of attenuation of correlations. Hence, the expansion of $\delta C(r) = \delta C\left(\delta h(r)\right)$ into a series of $\delta h(r)$ can be limited to the first term of series $\delta C = \chi(\delta h)^\delta$, where $\delta$ is a new critical index and $\chi$ is an expansion constant that generally depends on $\rho$ and $\theta$. Function $\left(\delta h(r)\right)^\delta$ determined in this manner has a pole on the order of $1/r^\delta$ at point $r = 0$. To eliminate this pole, we need

$$\delta C(r) = \begin{cases} \chi\left(\lambda^\eta e^{-\lambda r}/r\right)^\delta, & r > R^{(\infty)}, \\ 0, & r < R^{(\infty)}. \end{cases} \tag{34}$$

In other words, we assume that $\chi(r) = 0$ for $r < R^{(\infty)}$. Substituting this expression into Eq. (20), we obtain

$$\begin{aligned} \delta C_2 &= K_2\lambda^{\delta(1+\eta)-3}, \quad K_2(\rho, \theta) = \chi(\rho, \theta)\int_b^\infty e^{-\delta x}x^{2-\delta}dx, \\ \delta C_4 &= K_4\lambda^{\delta(1+\eta)-5}, \quad K_4(\rho, \theta) = \chi(\rho, \theta)\int_b^\infty e^{-\delta x}x^{4-\delta}dx, \end{aligned} \tag{35}$$

where $x = \lambda r$, $b = \lambda R^{(\infty)}$. For $\lambda \to 0$, the low boundary of the integrals $R^{(\infty)} = b/\lambda$ tends to infinity, while the interval of determined function $\hat{C}^{(\infty)}(k)$, $0 \le k \le k^{(\infty)}$, shrinks to zero.

Since $A = a\lambda^\eta$ and $\delta C_2 = K_2\lambda^{\delta(1+\eta)-3}$, the asymptotic OZ equation becomes

$$\frac{a}{4\pi\rho\lambda^{2-\eta}} = \frac{1}{4\pi\rho K_2\lambda^{\delta(1+\eta)-3}}. \tag{36}$$

Damping decrement $\lambda = \lambda(\Delta\rho, \Delta\theta)$ is a variable value in this equation and depends on $\Delta\rho$ and $\Delta\theta$. Equation (36) can thus be used only under the condition that critical indices $\eta$ and $\delta$ are interrelated by relation

$$2 - \eta = \delta(1 + \eta) - 3. \tag{37}$$

Under the above condition, both parts of Eq. (36) can be reduced by $\lambda^{2-\eta} = \lambda^{\delta(1+\eta)-3}$, transforming it into a definition of constant $a(\rho, \theta) = 1/K_2(\rho, \theta)$.

Formula (37) is well known in the theory of critical phenomena [1]. This is the first indication that the model we have chosen adequately depicts the phenomena that occur in the vicinity of critical point.

Based on Eq. (37), we obtain Eq. (36) in the form

$$\delta C_2(\Delta\rho, \Delta\theta) = K_2\lambda^{2-\eta}, \quad \delta C_4(\Delta\rho, \Delta\theta) = K_4\lambda^{-\eta}. \tag{38}$$

As a result, damping decrement $\lambda$ is equal to

$$\lambda = \sqrt{6\frac{\lambda^\eta(1 - 4\pi\rho C_2^{(0)}) + 4\pi\rho\lambda^2 K_2}{4\pi\rho\left(\lambda^\eta C_4^{(0)} - K_4\right)}};$$

after some rearranging of terms, it becomes

$$\lambda^{1-(\eta/2)} = \sqrt{\frac{6(1 - 4\pi\rho C_2^{(0)})}{4\pi\rho\left(\lambda^\eta C_4^{(0)} - (6K_2 + K_4)\right)}}. \tag{39}$$

## COORDINATES OF THE CRITICAL POINT

Relations found in this manner of course do not determine the exact value of $\delta C(r)$, since no concrete forms of functions $K_2(\rho, \theta)$, $K_4(\rho, \theta)$ are known. They nevertheless provide a number of useful results.

It is obvious that damping decrement $\lambda$ vanishes when $1 - 4\pi\rho C_2^{(0)} = 0$, and the asymptotic solution to the OZ equation takes the form $\delta h(r) = \dfrac{A}{(4\pi\rho)^2}\dfrac{1}{r}$. As a result, all integrals of function $\delta h(r)$ diverge at infinity, turning the critical point into the singularity of the statistical sum. According to Eq. (18), it contains

$$\begin{gathered}\frac{1}{\theta}\frac{\partial P}{\partial\rho} = (1-4\pi\rho C_2^{(0)}) + 4\pi\rho\delta C_2 = 0,\\ \frac{1}{\theta}\frac{\partial^2 P}{\partial\rho^2} = \frac{\partial(1-4\pi\rho C_2^{(0)})}{\partial\rho} + \frac{\partial[4\pi\rho\delta C_2]}{\partial\rho} = 0.\end{gathered}\tag{40}$$

Since $\delta C_2 = K_2\lambda^{2-\eta}$, the first and the second derivatives of the fluctuation component of pressure $\delta P$ in Eq. (40) vanish when $\lambda \to 0$:

$$\begin{gathered}\frac{1}{\theta}\frac{\partial\delta P}{\partial\rho} = K_2\rho\lambda^{2-\eta} \to 0,\\ \frac{1}{\theta}\frac{\partial^2\delta P}{\partial\rho^2} = K_2\rho 2\lambda^{1-\eta}\frac{\partial\lambda}{\partial\rho} + K_2\lambda^{2-\eta} \to 0.\end{gathered}$$

Formulas (40) then determine the coordinates of the critical point:

$$\begin{gathered}\frac{1}{\theta}\frac{\partial P^{(0)}}{\partial\rho} = 1-4\pi\rho C_2^{(0)} = 0,\\ \frac{1}{\theta}\frac{\partial^2 P^{(0)}}{\partial\rho^2} = \frac{\partial(1-4\pi\rho C_2^{(0)})}{\partial\rho} = 1 + 4\pi\rho\frac{\partial C_2^{(0)}}{\partial\rho} = 0.\end{gathered}$$

The position of critical point on the phase plane is thus determined only by the potential component of direct correlation function $C^{(0)}$; the fluctuation component has no effect on the coordinates of the critical point.

Differentiating Eq. (7) for pressure with respect to density and omitting the fluctuation term that has no effect on the coordinates of the critical point, we find that at the critical point,

$$\begin{gathered}\frac{\partial P}{\partial\rho} = \theta - 2\frac{1}{6}\rho\int_0^\infty r\frac{\partial\Phi(r)}{\partial r}G(r)4\pi r^2 dr\\ -\frac{1}{6}\rho^2\int_0^\infty r\frac{\partial\Phi(r)}{\partial r}\frac{\partial G(r)}{\partial\rho}4\pi r^2 dr = 0.\end{gathered}$$

Since attractive forces predominate when $r \to \infty$, the second integral in this equation, which contains derivative $\partial G/\partial\rho$, is always positive. Omitting it, we obtain inequality

$$Z_c = \frac{P_c}{\rho_c\theta_c} \le \frac{1}{2},\tag{41}$$

which determines all possible values of compressibility factor $Z_c$ at the critical point. As is clear from the data given in [16] for 23 different liquids, this is always valid (the maximum value is approached using quantum liquids for which $Z_c$ is 0.49; for other liquids, it is less than 0.3).

## COUPLING EQUATION FOR CRITICAL INDICES

In addition to Eq. (37) establishing the interrelation between critical indices $\eta$ and $\delta$, numerous similar formulas are known in the theory of critical phenomena. These formulas are usually obtained by means of thermodynamics [17], but some can be obtained directly from the OZ equation. Let us first consider equations of the second group.

Expanding damping decrement $\lambda(\rho,\theta)$ into a twofold series of powers of $\xi = \Delta\rho/\rho_c$ and $\tau = \Delta\theta/\theta_c$, and limiting ourselves to the two first terms, we obtain

$$\lambda = \xi^\mu + \tau^\nu + \ldots\tag{42}$$

(here we consider that $\lambda = 0$ at the critical point). Since the radius of correlation is found to be $R = 1/\lambda$, we have

$$R = \frac{1}{\xi^\mu + \tau^\nu}.\tag{43}$$

We now assume that we approach critical point $\xi = \chi\tau$ along a straight line where $\chi = \mathrm{const}$. The denominator in Eq. (43) in this case takes the form $\chi^\mu\xi^\mu + \tau^\nu = \tau^\nu\left(1 + \chi^\mu\tau^{\mu-\nu}\right)$. Since in this expression $\mu - \nu \approx 3$ (see below), the second term in parentheses can be ignored in the vicinity of the critical point. We thus obtain a relation that is well known in critical point theory: $R \sim \tau^{-\nu}$.

Let us assume that $\theta = \theta_c$. The following relations then hold in the vicinity of the critical point: $\frac{1}{\theta}\frac{\partial\delta P}{\partial\Delta\rho} = 4\pi\rho\delta C_2$, $\delta C_2 = K_2\lambda^{2-\eta}$, and $\lambda = \xi^\mu$. Combining these, we obtain $\frac{\partial\delta P}{\partial\xi} = \xi^{\mu(2-\eta)}$. Integrating this expression over $\xi$, we find that $\delta P = \xi^{(2-\eta)\eta+1}$. This equality can be written in standard terms of the theory of critical phenomena: $\delta P^{(\infty)} = \xi^\delta$. Therefore,

$$\delta = (2-\eta)\mu + 1.\tag{44}$$

Finally, since the isothermal compressibility is $\delta\kappa_\theta = \theta/(\partial\delta P/\partial\rho)$ and $\partial(\delta P)/\partial\rho \sim \lambda^{2-\eta} = (\xi^\mu + \tau^\nu)^{2-\eta}$, $1/\delta\kappa_\theta \sim \tau^{(2-\eta)\nu}$ on the isochor curve and $\delta\kappa_\theta \sim \tau^{-(2-\eta)\nu}$. Critical index $\gamma$, determined as $\delta\kappa_\theta \sim \tau^{-\gamma}$ in the theory of critical phenomena, is thus

$$\gamma = (2-\eta)\nu.\tag{45}$$

This formula is also well known in the theory of critical phenomena, so the applied approximation in this case also leads to correct relationships.

In addition to coupling equations, the theory of critical phenomena includes equations

$$\alpha + 2\beta + \gamma = 2, \quad \beta(\delta - 1) = \gamma,\tag{46}$$

and so on.

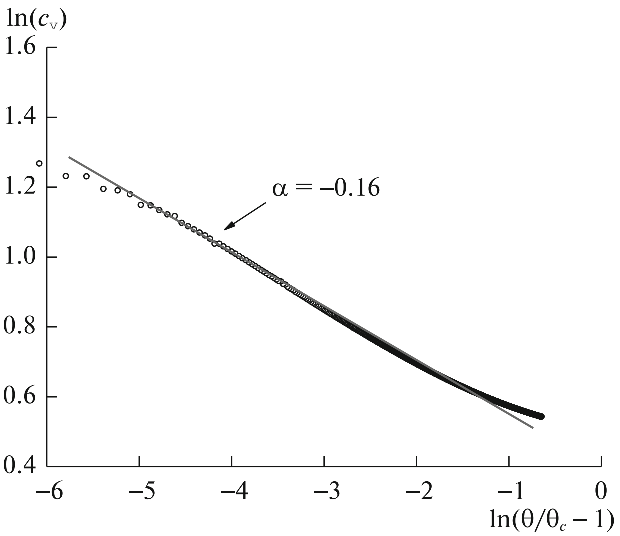

**Fig. 2.** Dependence of heat capacity $c_V$ on $\tau$ on a critical isochoric curve calculated using the OZ equation and closing equation $B = -(w - 1.2\rho\varphi)^2/2$, $\varphi = \Phi(r)/\theta$ for the LJ potential.

All of these equations were derived from thermodynamic inequalities by substituting ≥ for = [17]. This substitution is still considered to be insufficiently substantiated, so no appreciable attention was given to these relationships. However, let us recall that thermodynamics is a direct consequence of statistical mechanics [18]. Formulas (46), obtained using thermodynamics, must therefore be fitted by the same values of indices $\gamma$, $\delta$ and others included in the coupling equations derived from the OZ equations. This is possible only when = is used instead of ≥ in thermodynamic inequalities.

## CRITICAL INDICES $\alpha$ AND $\beta$

In addition to fluctuation indices $\mu$, $\nu$ and so on, thermodynamic coupling equations (47) also contain indices $\alpha$ and $\beta$, which cannot be obtained directly from the asymptotic OZ equation, since they are determined by the potential component of direct correlation function $C^{(0)}(r)$.

**Index $\alpha$.** As is well known, heat capacity at a constant volume is $c_V = \left.\frac{\partial e}{\partial\theta}\right|_\rho$, where the internal energy of the system is written as $e = e^{(0)} + \delta e$ in accordance with Eq. (9). It therefore follows that

$$c_V = \left(\frac{3}{2} + \frac{\partial\phi}{\partial\theta}\right) + \frac{1}{2}\rho\int_0^\infty \Phi_{(2)}(r) \times \frac{\partial G(r;\rho,\theta)}{\partial\theta}4\pi r^2 dr = c_V^{(0)} + \delta c_V. \qquad (47)$$

This formula contains two terms: potential and fluctuation components. To determine the contribution from fluctuation component $\delta c_V = \partial\phi/\partial\theta$, we must express $\delta c_V$ in terms of pressure $\delta P$ by means of Eq. (18). It is easy to show that the fluctuation component obtained in this manner is

$$\delta c_V = -\theta\int_{\rho_c}^{\rho_c+\Delta\rho}\frac{\partial^2(\delta P)}{\partial\theta^2}\frac{d\rho}{\rho^2} \to -\theta\frac{\partial^2(\delta P)}{\partial\theta^2}\frac{\Delta\rho}{\rho^2} \to 0 \quad \text{at} \quad \Delta\rho \to 0.$$

As a result, the heat capacity at the critical point is determined only by potential component

$$c_V^{(0)} = \frac{3}{2} + \frac{1}{2}\rho\int_0^\infty \Phi_{(2)}(r)\frac{\partial G(r;\rho,\theta)}{\partial\theta}4\pi r^2 dr, \qquad (48)$$

which depends entirely on the interaction potential.

For the LJ potential, calculations using Eq. (48) lead to the results shown in Fig. 2. It is obvious that over the range of temperatures from $\ln\tau \approx -4$ to $\ln\tau \approx -1$, formula $c_V \sim \tau^{-\alpha}$ with index $\alpha = 0.16$ provides a fairly accurate description of the obtained results. When $\tau \leq 5\times10^{-4}$, however, index $\alpha$ is reduced gradually, probably to scaling value $\alpha = 0.110$. Since experiments confirm this result (Table 2), we shall continue to assume that $\alpha = 0.11$.

**Index $\beta$.** Index $\beta$ is the power exponent in equality $\Delta\rho^{lv} = \rho^{lq} - \rho^{vp} = k\Delta\theta^\beta$, where $\rho^{lq}$ is the density of a liquid on the curve of liquid evaporation, and $\rho^{vp}$ is the density of vapor on the curve of vapor condensation.

It is obvious that for all isotherms $\Delta\theta = \theta - \theta_c = \text{const} \leq 0$, the condition of the equality of pressures of both phases $P_{lq} = P_{vp}$ must be met, or

$$P_{vp}^{(0)} + \delta P_{vp} = P_{lq}^{(0)} + \delta P_{lq}. \qquad (49)$$

In the first approximation, the fluctuation component of pressure is uniform on both branches of the bimodal, $\delta P_{vp} = \delta P_{lq}$, since the nature of fluctuation is the same in vapor and liquid. In this approximation, Eq. (49) is reduced to equality $P_{vp}^{(0)} = P_{lq}^{(0)}$. Each of the potential components of pressure $P^{(0)}$ in this equality can be expanded into twofold series of powers of density $\zeta$ and temperature $\tau$:

$$P^{(0)}(\zeta,\tau) = P_c^{(0)}(0,0) + b_1\tau + .. + a_3\zeta^3 + \ldots, \qquad (50)$$

where coefficients $a_k$, $b_k$ do not depend on $\zeta$ and $\tau$. Experiments clearly show that they are different on different sides of the critical point [12]. All terms with higher exponents of series (50) can be ignored when

$\zeta \to 0$, $\tau \to 0$, after which the equality takes the form $(a_3^{lq} - a_3^{v})\zeta^3 = (b_1^{v} - b_1^{lq})\tau$. Finding the cubic root of both parts of the equality, we find that

$$\rho_{lq} - \rho_v = -k\Delta\theta^{1/3} \quad \text{at} \quad \Delta\theta = \theta - \theta_c \le 0. \qquad (51)$$

For the pure potential version, critical index $\beta$ is thus $\beta^{(0)} = 1/3 = 0.333\ldots$.

However, the potential component does not determine the value of index $\beta$ completely: the fluctuation component also contributes to it, since the properties of the correlation sphere are differ slightly on either side of the critical point [12]. We therefore assume that

$$\beta = \beta^{(0)} + \delta\beta, \quad \text{where} \quad \beta^{(0)} = 0.333\ldots, \quad \delta\beta \ge 0. \qquad (52)$$

At present, it is impossible to calculate specific values of $\delta\beta$. We shall therefore consider $\delta\beta$ to be a fitting parameter; by varying it, we can seek agreement between the experimental data and theoretical predictions.

However, let us begin with an analysis of the experimental data. Ivanov noted that index $\beta$ “is most easily measured experimentally, since measurements of such complicated parameters as pressure can be avoided in this case” (see [12, p. 35]). We may therefore assume that the experimental values for the difference of $\beta_{\text{exp}}$ (Table 2) are the ones most reliable.

Table 1 shows the values of $\Delta\beta = \beta_{\text{exp}} - 0.333$ and the errors in measurements. It is clear that in the vast majority of cases, index $\beta$ is exactly equal to its potential value $\beta^{(0)} = 0.333$, and deviations $\Delta\beta \ge 0$ are almost always positive; when $\Delta\beta$ is negative, it is usually within the measurement error. Absolute value $\Delta\beta$ never exceeds 0.032; i.e., it is less than 10% of $\beta^{(0)} = 0.333$. Most important, however, by varying $\Delta\beta$ in the range $0 \le \Delta\beta \le 0.032$, we can achieve simultaneous agreement between the remaining critical parameters and their experimental values (see Table 2).

## CRITICAL INDICES $\gamma$, $\delta$, AND $\eta$

All of the remaining critical indices can be calculated using the known values of indices $\alpha$ and $\beta$ for coupling equations. This method of calculation is usually regarded as unreliable, since coupling equations have so far been derived by substituting $\ge$ for $=$ in thermodynamic inequalities. It is impossible to validate this substitution while remaining within the context of thermodynamics. As was noted above, however, this substitution is absolutely necessary within the model under consideration.

Let us therefore determine index $\nu$ using coupling equation $3\nu = 2 - \alpha$ (see Eq. (45)). Since we assume that $\alpha = 0.11$, index $\nu$ is always equal to 0.63 in this approximation.

Index $\gamma$ can be found by substituting known values of $\alpha$ and $\beta$ into identity $\gamma = 2 - \alpha - 2\beta$ (see Eq. (46)). We used only the fluctuation component $\delta\beta$ of the index $\beta$ as the fitting parameter to calculate the critical indices given in Table 2; if the values of index $\alpha$ are varied slightly, we can obtain more precise values of the remaining indices.

Index $\delta$ can be calculated using relation $\delta = 1 + (\gamma/\beta)$ with known values $\gamma$ and $\beta$ (see Eq. (46)). Finally, index $\eta$ can be calculated with Eq. (37): $\eta = (5 - \delta)/(1 + \delta)$, using known value $\delta$. The resulting values are given in Table 2.

The first thing we notice upon closer examination of Table 2 is that the experimental data almost always differ from the values predicted by the scaling theory. In addition, the discrepancies between theory and experiment almost always significantly exceed the measurement error. At the same time, simultaneous agreement between the theoretical values of indices $\gamma$, $\delta$, $\eta$ and the experimental data can be achieved[7] by slightly varying $\beta^{(\infty)}$ in the formula $\beta = 0.333 + \beta^{(\infty)}$ within the context of fluctuation theory (though it is not always clear which data should be considered “experimental values,” since different authors report strongly different values of these indices).

Special attention must be given to $SF_6$. Table 2 contains the value $\delta = 4.99$ [2] for this substance. However, the anomalously low magnitude of $\eta = 0.002$ corresponds to this value of $\delta$. It is therefore likely that the value $\delta = 4.99$ in Table 2 was determined with a high degree of error. At the same time, the values of other indices were found for $SF_6$ [12]: $\beta = 0.3508 \pm 0.0013$, $\gamma = 1.16 \pm 0.03$, $\delta = 4.30 \pm 0.01$, and $\eta = 0.130$–$0.131$. The author has emphasized that these data were measured “especially precisely.”

These index values differ notably from those predicted by the scaling theory ($\beta = 0.3245$, $\gamma = 1.2390$, $\delta = 4.818$, $\eta = 0.0312$). At $\beta = 0.352$ and $\Delta\beta = 0.018$ (which lie within the measurement error), calculations of indices $\gamma$, $\delta$, and $\eta$ using coupling equations yield $\gamma = 1.19$, $\delta = 4.38$, $\eta = 0.11$, which is much closer to the experimental data on these indices. Slight variations of $\alpha$ provide the best coincidence with the experiment.

## CONCLUSIONS

We first assumed that critical phenomena are generated by the fluctuation waves of density that exist in each equilibrium system. Since these waves are described by equations of hydrodynamics [7], it is

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[7] This requirement was established in a monograph by Stanley [17].

impossible to introduce them directly into the Gibbs equilibrium theory. We can nevertheless characterize their contributions in terms of average kinetic energy $\theta\phi$ per particle and consider this contribution in the canonical distribution. Our hypothesis showed that all thermodynamic parameters of the system are equal to the sum of two terms: the potential and the fluctuation components.

This model allowed us to:

(1) explain the mechanism behind the onset of crossover;

(2) explain the Ivanov effect;

(3) derive equations that determine the coordinates of critical points in real liquids;

(4) show that the compressibility factors of all liquids $Z_c = P_c/\rho_c\theta_c$ are always less than 1/2 at a critical point;

(5) derive all known coupling equations for different critical indices;

(6) use coupling equations for calculating the critical indices of 15 liquids with accuracy exceeding that of scaling theory predictions of these indices. Only one fitting factor, ranging from 0 to 10% of the main value of $\beta$, was used for the simultaneous determination of five different indices of one liquid.

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