LIQUIDS AND LIQUID CRYSTALS

CRITICAL PHENOMENA IN FILLED LIQUID SYSTEMS

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We consider the filled liquid system at a close vicinity of the critical point. To find its pair correlation function and the correlation length of order parameter (density) fluctuations, we use the Ornstein—Zernike (OZ) approximation. We show that the presence of macroscopic impurities causes shifts of the critical temperature and density in the system, and even a low impurity concentration can cause significant changes of critical parameters. We also find the analogy of the filled liquid system with a finite-size system.

1. Introduction

Critical phenomena in simple fluids are studied well at the moment [1]. Nevertheless, we have poor information about peculiarities of the critical state in filled liquid systems. Here, we mean macroscopic hard-body impurities distributed in liquid. On the other hand, we know that, in the critical state, even insignificant perturbations can cause a strong reaction of the system. From this point of view, when investigating the critical phenomena in liquids, it is necessary to take into account the presence of impurities. The behavior of the system in this case depends radically on the chemical characteristics of impurities especially at a close vicinity of the critical point.

The system to be studied in our research is a fluid with impurities homogeneously distributed over the sample. We suppose that liquid does not interact with the surfaces of impurity particles. We investigate the correlative behavior of this system by finding the pair correlation function of density fluctuations. The OZ theory [2] will be helpful. The presence of impurities is accounted as regions without fluid, i.e. we consider the excluded-volume effect.

By using the integral OZ equation and keeping in mind a homogeneous distribution of impurities, we find the pair correlation function of density fluctuations. Knowing the pair correlation function, it is possible to calculate the correlation length as well. Comparing it with the correlation length of a pure liquid, we suppose to obtain shifts of the critical parameters (temperature and density) for the filled system. We compare the results with similar data on finite-size systems.

2. Pair Correlation Function

In order to investigate this problem, we use the OZ integral equation

$$G_2(r) = f(r) + \int \rho(r_1)f(r_1)G_2(|\vec{r} - \vec{r}_1|)d\vec{r}_1, \qquad (1)$$

where $G_2(r)$ and $f(r)$ are the pair and direct correlation functions, respectively, and the density $\rho(r) = \langle\rho\rangle =$ const for an isotropic pure liquid system. For a filled fluid (i.e. liquid with impurities), it is natural to consider the expression for the density as follows:

$$\rho(\vec{r}) = \langle\rho\rangle \left(1 - v_0 \sum_n \delta(\vec{r} - \vec{r}_n)\right), \qquad (2)$$

where $\vec{r}_n$ determines positions of impurity particles and v_0 is the volume of an impurity particle. Here, we stress again that the distribution of impurity particles is supposed to be homogeneous. So, in view of relation (2), Eq. (1) yields

$$G_2(r) = f(r) + \langle\rho\rangle \int f(r_1)G_2(|\vec{r} - \vec{r}_1|)d\vec{r}_1 -$$

$$-v_0 \langle\rho\rangle \sum_n f(\vec{r}_n)G_2(|\vec{r} - \vec{r}_n|). \qquad (3)$$

Using the Taylor expansion for the pair correlation function from Eq. (3), we find the differential equation

$$\Delta G_2(r) - \kappa^2 G_2(r) - \varepsilon^2 \sum_n f(\vec{r}_n) G_2(|\vec{r} - \vec{r}_n|) =$$

$$= -f(r)/C_2, \tag{4}$$

where $\kappa^2 = (1 - C_0)/C_2$, $C_0 = \langle \rho \rangle \int f(r) d\vec{r}$ and $C_2 = \langle \rho \rangle /6 \int f(r) r^2 d\vec{r}$ are the zero and second spatial moments of the direct correlation function, $\varepsilon^2 = v_0 \langle \rho \rangle /C_2$. By the way, we can get the differential OZ equation for an isotropic pure liquid system from (4) if we formally take $\varepsilon^2 = 0$. After the Fourier transformation, we have

$$(q^2 + \kappa^2 + \varepsilon^2 \sum_n f(\vec{r}_n) \exp(-i\vec{q}\vec{r}_n)) G_2(q) = f(q)/C_2. \tag{5}$$

Using the approximation $f(r) = C_0 \delta(r)/\langle \rho \rangle$ for the direct correlation function, it is possible to get the Fourier image of a pair correlation function from (5) as

$$G_2(q) = \frac{C_0}{\langle \rho \rangle C_2 (q^2 + \kappa^2 + \varepsilon^2 \sum_n f(\vec{r}_n) \exp(-i\vec{q}\vec{r}_n))}. \tag{6}$$

For an isotropic pure infinite system (i.e. when $\varepsilon^2 = 0$), the well-known formula for a pair correlation function of density fluctuations can be deduced from Eq. (6) in the form

$$G_2(r) = \frac{C_0 \exp(-\kappa r)}{4\pi \langle \rho \rangle C_2 r}, \tag{7}$$

and κ^{-1} determines the correlation length of the infinite pure liquid system. Equation (6) depends strongly on the distribution of impurity particles, i.e. on $\{\vec{r}_n\}$. For the most simple situation of an isotropic system, the sum in (6) can be transformed to an integral. Namely, if we denote the impurity volume concentration as σ, then we can take

$$\sum_n f(\vec{r}_n) \exp(-i\vec{q}\vec{r}_n) \to$$

$$\to \sigma \int f(r) \exp(-i\vec{q}\vec{r}) r^2 \sin \theta dr d\theta d\varphi. \tag{8}$$

In this case, we have the following:

$$\int f(r) \exp(-i\vec{q}\vec{r}) r^2 \sin \theta dr d\theta d\varphi =$$

$$= \frac{4\pi}{q} \int f(r) r \sin(qr) dr. \tag{9}$$

Moreover, we also use the Taylor approximation for a sine:

$$\frac{4\pi}{q} \int f(r) r \sin(qr) dr \approx \frac{4\pi}{q} \int f(r) r (qr - q^3 r^3/6) dr =$$

$$= \frac{C_0 - q^2 C_2}{\langle \rho \rangle}. \tag{10}$$

From Eq. (6), we can get

$$G_2(q) = \frac{C_0}{\langle \rho \rangle C_2 (q^2(1 - x) + \kappa^2 + x C_0)} =$$

$$= \frac{C_0}{(1 - x) \langle \rho \rangle C_2 (q^2 + \kappa_*^2)}, \tag{11}$$

where $\kappa_*^2 = \frac{1 - (1 - x)C_0}{(1 - x)C_2}$ and $x = \sigma v_0$. After that, we can easily calculate the pair correlation function for the system with impurities as

$$G_2(r) = \frac{C_0 \exp(-\kappa_* r)}{4\pi \langle \rho \rangle (1 - x) C_2 r}. \tag{12}$$

Expression (12) for the pair correlation function of a filled system similar to the expression for that of a pure liquid (see Eq. (7)). But, in comparison with a pure liquid, shifts of the critical parameters take place in a filled system. We will show this in the next section.

3. Shifts of the Critical Parameters

At a a close vicinity of the critical isochor for a pure infinite system, the dependence of the parameter κ on temperature is of scaling form [1,3]

$$\kappa = \kappa_0 \tau^v, \tag{13}$$

where $\kappa_0 = $ const, $\tau = (T - T_C)/T_C$ is a deviation of temperature from its critical value T_C and $v = 0.625$ is the critical index. As a result, the correlation length $R_C = \kappa^{-1}$ at the growth of the critical temperature $T = T_C$ to infinity.

For a system with impurities, the correlation length

$$R_{C*}^2 = \kappa_*^{-2} = \frac{1 - x}{\kappa^2 + x C_0/C_2}. \tag{14}$$

So even when $\kappa = 0$ (i.e. at the critical point of a pure system when $T = T_C$), the correlation length is of finite value. This means that the presence of impurities leads to a shift of the critical temperature. The new critical temperature T_C^* can be found from Eq. (14)

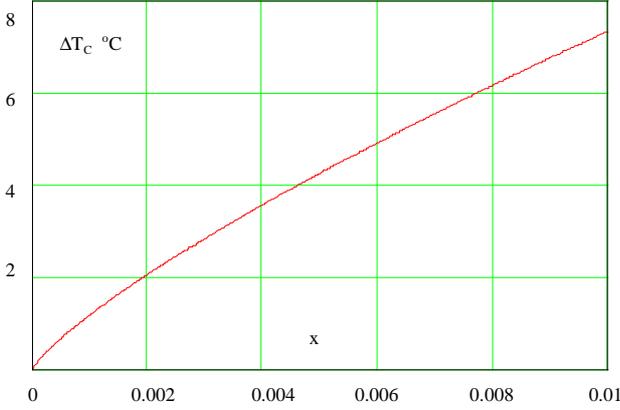$$T_C^* = \frac{T_C}{1 + (x C_0/\kappa_0^2 C_2)^{1/2v}}, \tag{15}$$

Fig. 1. Dependence of the critical temperature shift on the parameter x

Fig. 2. Dependence of the critical density shift on the parameter x

and the shift of the critical temperature is

$$\Delta T_C = T_C - T_C^* = \frac{T_C}{1 + (xC_0/\kappa_0^2 C_2)^{-1/2v}}. \tag{16}$$

Comparing formula (15) with the expressions for the critical temperature of a finite-size system (see, for example, [4,5]), we can conclude that the parameter

$$L = \sqrt{C_2/xC_0} \tag{17}$$

determines "the linear size" of a filled system. It is well known that the system can be mentioned as a finite-size one if the correlation length is comparable with the linear size of the system [6]. For a system with impurities, such typical size is determined by Eq. (17). Really, if $x \to 0$, then $L \to \infty$, and the system can be treated as infinite. So we can neglect the presence of impurities if

$$\frac{xC_0}{\kappa_0^2 C_2} \ll 1 \tag{18}$$

or just the same in another way:

$$x \ll \frac{C_2 \kappa_0^2}{C_0} \equiv \lambda. \tag{19}$$

Here, the parameter λ characterizes the liquid. If $\lambda \gg 1$ (this situation can be realized in fluids with strong intermolecular interaction), even significant concentrations of impurities can be neglected, and we can consider the system as a pure liquid.

In a close vicinity of the critical isotherm ($\tau \ll \Delta\rho^{1/\beta}$), we consider the scaling dependence of the parameter κ on the density ρ [1,3]:

$$\kappa(\rho) = \kappa_0 \Delta\rho^{v/\beta}. \tag{20}$$

Here, $\Delta\rho = (\rho - \rho_C)/\rho_C$ is a deviation of the density from its critical value, and $\beta = 0.33$ is the critical
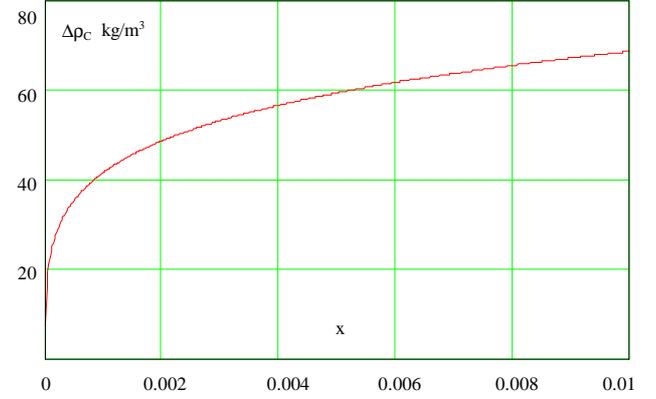
index. Then the new critical density ρ_C^* for a system with impurities is

$$\rho_C^* = \frac{\rho_C}{1 + (xC_0/\kappa_0^2 C_2)^{\beta/2v}}. \tag{21}$$

So, the shift of the critical density is

$$\Delta\rho_C = \rho_C - \rho_C^* = \frac{\rho_C}{1 + (xC_0/\kappa_0^2 C_2)^{-\beta/2v}}. \tag{22}$$

In Figs. 1 and 2, shifts of the critical parameters (temperature and density, respectively) as functions of the parameter x are presented. It was taken $T_C = 300$ K, $\kappa_0 = 1$ nm^{-1}, $\sqrt{C_2/C_0} = 1$ nm and $\rho_C = 300$ kg·m^{-3}. It can be seen that, even for small values of x, the shifts are significant enough. For example, if $x = 0.001$, the temperature shift $\Delta T_C = 1.2$ °C and the shift of the critical density in this case $\Delta\rho_C = 41.7$ kg·m^{-3}.

Using the scaling dependence of the parameter κ on temperature and density, we can derive the dependence of the correlation length on the temperature, density, and concentration of impurities (more precisely, on the parameter x) as well (see Figs. 3 and 4). It is clearly seen that, under $x \neq 0$ at the critical point of a pure liquid (i.e. $T = T_C$ or $\rho = \rho_C$), the correlation length is of finite value.

4. Conclusions

Thus, the presence of impurities significantly changes the behavior of a liquid system. The most considerable effect is shifts of the critical parameters (i.e. temperature and density). The dependence of these shifts on the impurity concentration σ (more precisely on the parameter $x = \sigma v_0$) is of scaling-law form, and a filled system (i.e. a system with impurities) can be treated as
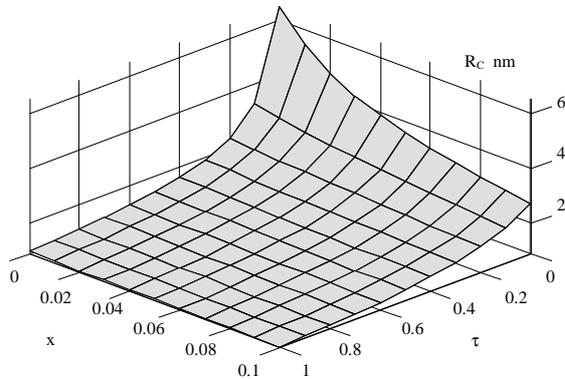
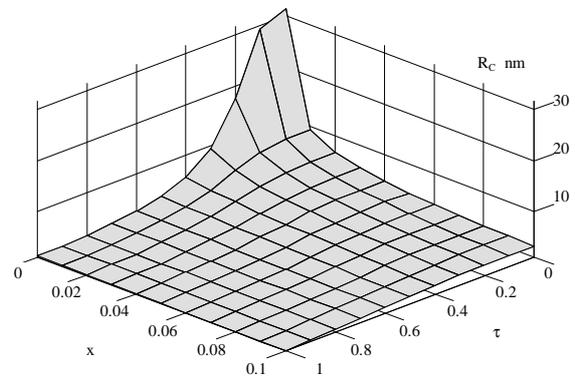Fig. 3. Dependence of the correlation length on temperature and the parameter x

Fig. 4. Dependence of the correlation length on density and the parameter x

spatially finite-size or as a system with reduced dimension.

1. *Anisimov M.A.* Critical Phenomena in Liquids and Liquid Crystals.— Moscow: Nauka, 1987 (in Russian).

2. *Munster A.* The Theory of Fluctuations. — New York: Academic Press, 1959.

3. *Patashinskii A.Z., Pokrovskii V.L.* The Fluctuation Theory of Phase Transitions. — Oxford: Pergamon Press, 1979.

4. *Chalyi A.V., Chernenko L.M.* Phase Transition in Finite-Size Systems and Synaptic Transmission. — New York: Nowa Science, 1993.

5. *Chalyi A.V.* // J. Mol. Liquids, 58 (1993) 179.

6. *Fisher M.E.* // Phys. Rev. 176 (1968) 257.

КРИТИЧНІ ЯВИЩА В РІДКІЙ СИСТЕМІ З ДОМІШКАМИ

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Р е з ю м е

Розглянуто однокомпонентну рідку систему з домішками. Для отримання парної кореляційної функції та радіуса кореляції параметра порядку (густини) в околі критичної точки такої системи використано наближення Орнштейна—Церніке. Показано, що наявність макроскопічних домішок приводить до зміни критичної температури та густини і навіть незначні концентрації домішок можуть спричинити суттєві зміщення критичних параметрів. Простежується аналогія між системою з домішками і просторово обмеженою системою.