INFLUENCE OF GRAVITATION ON THE HEAT CAPACITY OF LIQUIDS IN THE CRITICAL REGION

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The theoretical calculation of the heat capacity of a one-component liquid in a gravitational field near the critical point is carried out. The shift of the temperature, which corresponds to the maximum of the averaged-over-height heat capacity of a spatially inhomogeneous liquid, relative to the critical temperature of a homogeneous liquid in the absence of an external field is determined. The specific calculations are executed for the vicinities of a critical isohore and a critical isotherm.

Introduction

External fields blur the second-order phase transition attenuating an interaction of fluctuations [1—3]. The critical state of the liquid with an anomalous behavior of physical properties, which is typical of infinite-size systems without external fields, becomes actually unachievable in the presence of external fields. In similar situations, one could claim that the kind of the phase transition is changed, i.e. it isn't a second-order phase transition anymore (or, more precisely, a continuous phase transition), and it becomes the first-order phase transition where no anomalous interaction between fluctuations of the order parameters of the system under study is present.

All the above-mentioned concerns also liquids in a gravitational field in full measure. Under the influence of a gravitation, a spatial inhomogeneity of various physical quantities appears near the critical point — thermodynamic (susceptibility, heat capacity, etc.), kinetic (the coefficients of viscosity, diffusion, heat conductivity, etc.), and correlation quantities (correlation functions and correlation lengths of order parameters) (see, for example, [4]). Properly saying, the critical state of a one-component liquid which is isomorphic to the critical phenomena in second-order phase transitions in the Ising model in a zero magnetic field is theoretically implemented only at the mathematical level, where the density of a liquid takes on precisely the critical value. At the same time, there is a certain vicinity (a range of heights) of the exactly critical state where the scaling laws of the fluctuation theory of phase transitions should be experimentally revealed [2]. Furthermore, the investigation of the critical behavior of liquids in the critical region taking into account the influence of a gravitation or the so-called "gravitation effect" gives us a unique opportunity to study the dependences of properties of liquids not only on temperature, but also on "field" variables. Namely such investigations have been carried out for a long time at the Chair of Molecular Physics of Taras Shevchenko Kyiv National University [3—6].

The objective of the present work is to calculate both the heat capacity of a one-component liquid in a gravitational field near the critical point and the shift of the temperature that corresponds to the averaged-over-height heat capacity in such a spatially inhomogeneous liquid relative to the critical temperature of a homogeneous liquid. This calculation will be carried out both for the vicinities of a critical isochore and a critical isotherm.

1. Specific Heat of a Liquid Near the Critical Point

The temperature dependence of the isochoric specific heat of a liquid near the critical point is generally approximated by the power dependence (see, for example, [7])

$$C_v = C_{v0} + A\tau^{-\alpha}, \quad (1)$$

where the first term defines the regular part of the specific heat which has no singularities in the critical region including also the critical point itself, while the second term describes the singular part of a heat capacity which is concerned with a strong interaction between fluctuations of a liquid near the critical point. In the second term of Eq. (1), the following notations are used: A is the constant non-universal quantity, whose values depend on a liquid nature; $\tau = (T - T_c)/T_c$ is the deviation of a temperature from the critical value; and α is the universal critical index which depends on a spatial dimension, the dimension (the number of components) of an order parameter, and the symmetry of a Hamiltonian. For the liquids which are isomorphic to the 3-dimensional Ising model, $\alpha \approx 0.1$.

In the fluctuation (scaling) theory of critical phenomena [4, 7], the singular part of a specific heat C_{vs} is described by the scaling formula

$$C_{vs} = \tau^{-\alpha} f(\varphi/\tau^{\beta}), \quad (2)$$

where φ is the order parameter (for a one-component liquid, its role is played by a deviation of the density from the critical value $\varphi = \Delta\rho = (\rho - \rho_c)/\rho_c$); β is the critical index which equals approximately 1/3 for Ising-like systems; and $f(x)$ is the scaling function which has the following asymptotes: a) $f(x \to 0) = A$ in the close vicinity of a critical isochore where the strong inequality $\varphi << \tau^{\beta}$ holds; b) $f(x \to \infty) = Ax^{-\alpha/\beta}$ in the close vicinity of a critical isotherm where the opposite strong inequality $\varphi >> \tau^{\beta}$ holds.

Because of the influence of Earth's gravitational field, a liquid becomes spatially inhomogeneous near the critical point. Under experimental conditions, various mixers are frequently used to avoid a spatial inhomogeneity of a liquid, but it is clear that this is the artificial procedure that isn't inherent in natural conditions. For a spatially inhomogeneous liquid, the order parameter φ becomes a function of the field variable z which is conjugated to the order parameter in the thermodynamic sense. In the theory of the gravitational effect [3–6], $z = \rho_c gh/P_c$, where ρ_c and P_c are the critical density and the pressure, g is the gravitational acceleration, and h is the height which is usually counted off from the level with a critical density. The dependence $\varphi(z)$ has a power behavior on the critical isotherm,

$$\varphi(\tau = 0, z) = Dz^{1/\delta}, \quad (3)$$

where D is one more non-universal constant and δ is the critical index whose numerical value is close to 5 for Ising-like liquids.

Taking into account Eqs. (2) and (3), the local (at a certain height) value of the specific heat C_{vs} of a liquid at the given deviation of a temperature from the critical temperature is

$$C_{vs} = \tau^{-\alpha} f_1(z/\tau^{\beta\delta}). \quad (4)$$

Moreover, the scaling function $f_1(y)$ has the following asymptotes which should be in accord with the above-presented formulae: a) $f_1(y \to 0) = A$ in the close vicinity of a critical isochore, where the strong inequality $z << \tau^{\beta\delta}$ holds; b) $f(x \to \infty) = Ax^{-\alpha/\beta}$ in the close vicinity of a critical isotherm, where the opposite strong inequality $\varphi >> \tau^{\beta}$ holds.

2. Shift of the Critical Temperature near the Critical Isochore

Hereinafter, the critical temperature shift will be understood as a change of the temperature at which the maximum of the heat capacity of an inhomogeneous liquid averaged over a certain layer is realized relative to the critical temperature, at which the maximum of the specific heat of a homogeneous liquid is achieved. Let us examine the average value of the specific heat C_{vs} of a one-component liquid that can be obtained by integrating the local value (4) over the certain layer $-z_0 \le z \le z_0$ of a liquid that is near the critical isochore,

$$\langle C_{vs} \rangle = \frac{1}{2z_0} \int_{-z_0}^{z_0} C_{vs}(\tau, z) dz = \tau^{-\alpha} F(y_0), \quad (5)$$

where $F(y_0)$ is the corresponding scaling function of the argument $y_0 = z_0/\tau^{\beta\delta}$. We note that the middle of a layer $z = 0$ corresponds to the level with the critical density, $\rho = \rho_c$.

Certainly, the value of temperature at the maximum of the specific heat C_{vs} which is computed from Eq. (5) and corresponds to the value averaged over a layer of a liquid in the gravitational field doesn't coincide with the value of critical temperature for the heat capacity C_{vs} which is calculated from Eqs. (1) and (2). Indeed, according to Eq. (1), the maximum of the isochoric specific heat C_{vs} is achieved at the critical temperature $T = T_c$, when $\tau = 0$. The same result follows from Eq. (2), because, according to the extremum condition for the temperature derivative of heat capacity, we have

$$\tau_m = -\left(\frac{\beta\delta}{\alpha}\frac{f'(y)}{f(y)}y\right)^{1/\beta\delta}, \quad (6)$$

where τ_m is the temperature deviation that corresponds to the heat capacity maximum. Then, a heat capacity maximum is realized when $\tau_m = 0$, i.e. at the critical temperature $T = T_c$ at the level $z = 0$ where the density achieves the critical value. For both Eqs. (1) and (2), the singular part of the isochoric specific heat C_{vs} takes on an infinite value. Certainly, this is some approximation, since the indicated equations don't take into account effects of the spatio-temporal dispersion.

On the other hand, the averaged value of the specific heat, $\langle C_{vs}\rangle$ which is determined from Eq. (5) has an extremum (a maximum) at a quite different temperature τ_m^* which is determined by the formula

$$\tau_m^* = -\left(\frac{\beta\delta}{\alpha}\frac{F'(y_0)}{F(y_0)}y_0\right)^{1/\beta\delta}. \tag{7}$$

This yields that a) the quantity τ_m^* cannot be equal to zero, since the half-width z_0 of the plane layer, from which the information about the averaged value of a heat capacity is read, is always nonzero; b) the quantity τ_m^* is negative. In other words, the last means that if the average density of a plane layer equals the critical density, the maximum of the singular part of the specific heat of an inhomogeneous liquid in the gravitational field is achieved at some temperature T_c^* which can be conditionally referred as the "critical temperature" of an inhomogeneous liquid, as mentioned above. Moreover, $T_c^* < T_c$, where T_c is the critical temperature of a homogeneous liquid in the absence of external fields. Therefore, in order to take into account the effect of averaging the specific heat, it is natural to count off the temperature T not from the critical temperature T_c of a homogeneous liquid in the absence of external fields, but from the temperature T_c^* which determines the maximum of the specific heat of an inhomogeneous liquid.

Taking into account all the mentioned above, let us find a dependence between the critical temperatures T_c^* and T_c. To this end, we use the condition that, according to (5), the averaged value of a specific heat should be equal to the specific heat which is characterized by (4) at the temperature shift $\tau^* = (T - T_c^*)/T_c^*$, i.e.

$$\tau^{-\alpha}F(y_0) = \tau^{*-\alpha}f(y). \tag{8}$$

It follows from here that $\tau^*/\tau = [F(y_0)/f(y)]^{-1/\alpha}$ or $\Delta T_c = \Delta T[F(y_0)/f(y)]^{-1/\alpha}$, where such notations are used: $\Delta T_c = T_c^* - T_c$, $\Delta T = T - T_c$.

Let us determine the explicit dependence between T_c^* and T_c by using the well-known expression for the asymptotics of a scaling function $f(y)$ from formula (4) near the critical isochore (see, for example, [3, 4])

$$C_{vs}(\tau, z) = A\tau^{-\alpha}\left(1 + A_1\frac{|z|}{\tau^{\beta\delta}}\right). \tag{9}$$

Then, for the average value of specific heat in a $2z_0$-thick plane layer, whose middle is at the level $z = 0$ with the critical density, we get

$$\langle C_{vs}\rangle = \frac{1}{2z_0}\int_{-z_0}^{z_0} C_{vs}(\tau, z)dz = A\tau^{-\alpha}\left(1 + A_1\frac{|z_0|}{2\tau^{\beta\delta}}\right). \tag{10}$$

On the other hand, at the level $z = 0$ with the critical density, such a specific heat is determined by formula (4) provided that the temperature shift τ is replaced by τ^* and the scaling function is $f_1(0)= A$. As a result, we get

$$\tau^{-\alpha}\left(1 + A_1\frac{|z_0|}{2\tau^{\beta\delta}}\right) = \tau^{*-\alpha}. \tag{11}$$

It is worth to note that, when the width of a plane layer increases, the average value of a specific heat should decrease, since the interval of heights over which we average in formula (10) covers the levels with density that moves away from the critical one. This means that A_1 is negative in formulae (9)—(10). Taking into account these circumstances and the inequality $|z|/\tau^{\beta\delta} << 1$ which characterizes the vicinity of the critical isochore, we get, after simple transformations, the following formula for the temperature shift $\Delta T_c = T_c^* - T_c$ induced by gravitation:

$$\Delta T_c = -T_c\left(\frac{|A_1 z_0|}{2\alpha}\right)^{1/\beta\delta}. \tag{12}$$

To derive (12), it is necessary to set $\tau^* = 0$ in relation (11), i.e. $T = T_c^*$, which gives us the following value for a temperature shift: $\tau = (T_c^* - T_c)/T_c$. The result obtained justifies once more the fundamental conclusion which follows from (7) on that $\Delta T_c < 0$, i.e. $T_c^* < T_c$. In addition to this qualitative result, we also present the quantitative estimation of the value of a shift of the critical temperature by formula (12). For classical liquids such as benzene, pentane, carbon dioxide, etc. with relatively high critical temperatures $T_c \sim 300 \div 400$ K, we have the following estimation for the critical temperature shift taking into account experimental values of the parameters $\alpha \approx 0.1$ and $|A_1| \approx 1$ (see, for example, [4, 7, 8]) in the vicinity of the critical isochore when $z_0 \approx 10^{-6}$, $\Delta T_c \approx 10^{-2}$ K.

For quantum liquids such as He^4 near the λ-point ($T_\lambda \approx 2.17$ K), it was achieved such a closeness to the λ-transition point in experiments [9, 10]: $(T - T_\lambda)_{\min} \approx$

10^{-8} K and $(T-T_\lambda)_{\min} \approx 2 \cdot 10^{-8}$ K, respectively. The critical index a which describes the experimental data obtained in work [11] in the best way is $\alpha \approx 0.013$. By keeping values of the other parameters in (12) to be fixed, we obtain the following approximate values of shifts of the λ-transition temperature for He^4 in the vicinity of the critical isochore: $\Delta T_\lambda = T_\lambda^* - T_\lambda \approx -(10^{-7} \div 10^{-8})$ K.

3. Critical Temperature Shift near the Critical Isotherm

The singular part of the specific heat of an inhomogeneous liquid in the gravitational field near the critical isotherm is described by the following formula:

$$C_{vs} = B_0 z^{-\alpha/\beta\delta}(1 + B_1\tau/z^{1/\beta\delta}). \tag{13}$$

To deduce it, we used the well-known asymptotics of a scaling function $f_1(y)$ when $\tau^{\beta\delta} << z$ [3—5, 7]. Because, when moving away from the level $z=0$ with the critical density, a specific heat should decrease according to evident physical reasons, the constant B_1 in formula (13), as well as the constant A_1 in formula (9), is negative.

Let us find the average value of the specific heat of an inhomogeneous liquid in the plane layer $z_1 \le z \le z_2$

$$\langle C_{vs}\rangle = \frac{1}{\Delta z}\int_{z_1}^{z_2} C_{vs}(\tau, z)dz =$$

$$= \frac{B_0}{\Delta z}\left(\frac{z_2^m - z_1^m}{m} - |B_1|\tau\frac{z_2^n - z_1^n}{n}\right), \tag{14}$$

where $\Delta z = z_2 - z_1$ is the layer width and the exponents $m = 1 - \alpha/\beta\delta \approx 0.94$ and $n = 1 - (1+\alpha)/\beta\delta \approx 1/3$.

Let us introduce the coordinate of the middle of the plane layer $\zeta = (z_1 + z_2)/2$ which satisfy the condition $\tau^{\beta\delta} << \zeta$. Then, based on the same arguments as the foregoing ones for a vicinity of the critical isochore, we arrive at the following formula for the critical temperature shift for an inhomogeneous liquid under the influence of a gravitation:

$$\Delta T_c = T_c^* - T_c = \frac{T_c T_c^*}{|B_1|\left(\tau\varsigma^{-\frac{1}{\beta\delta}}\right)} \times$$

$$\times \left[m(m+1) - |B_1|\left(\tau\varsigma^{-\frac{1}{\beta\delta}}\right) n\,(n+1)\right]\left(\frac{\Delta z}{\varsigma}\right)^2. \tag{15}$$

When $|B_1| \approx 1$ and $\tau/\zeta^{1/\beta\delta} \approx 0.1$, the expression in square brackets in (15) is negative and equals 0.04 in absolute value. For the classical liquids with critical temperatures $T_c \approx 300$ K and in the case where the maximum temperature is close to the critical temperature, $\tau_{\min}{\approx}10^{-5}$, we have $\Delta T_c \sim -10^{-3}$ K. To obtain this estimation, we took $\tau^{\beta\delta}{\approx}10^{-8}$ and $\zeta \approx (\tau/0.1)^{\beta\delta}{\approx}10^{-6.5}$, while the dimensionless linear size of a specimen, along which we averaged, is $\Delta z{=}\rho_c g\Delta h/P_c{\approx}10^{-(9-10)}$.

The results obtained in the present work will be used later on to compare two effects — the influence of a gravitation on the critical temperature and the competing influence of a spatial limitation of a liquid system.

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ВПЛИВ ГРАВІТАЦІЇ НА ТЕПЛОЄМНІСТЬ РІДИН
У КРИТИЧНІЙ ОБЛАСТІ

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Р е з ю м е

Проведено теоретичний розрахунок теплоємності однокомпонентної рідини в гравітаційному полі поблизу критичної точки. Знайдено зсув температури, яка відповідає максимуму усередненої за висотою теплоємності просторово неоднорідної рідини, по відношенню до критичної температури однорідної рідини у відсутності зовнішнього поля. Конкретні розрахунки виконано як для околу критичної ізохори, так і для околу критичної ізотерми.