HEAT CAPACITY AND THE SHIFT OF THE CRITICAL TEMPERATURE IN CONFINED LIQUIDS

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An analytical expression for the heat capacity of confined one-component liquid in its critical region has been obtained, and a new value of the critical temperature, which corresponds to the maximum of the heat capacity of such liquid, has been determined. The obtained results have been applied to the studies of the influence of the system confinement on the specific heat of He^4 in the vicinity of its λ-point. The relevant experimental results, obtained under the microgravitation condition during the flight of the Space Shuttle in 1997, were taken as a reference point. The problem of competition between two effects, the gravitation and finite-size ones, on the critical temperature of the confined system has been considered. Theoretical estimations of those two factors, when calculating the temperature shift of the λ-transition point in He^4, give rise to results of the same sign and quite close by the absolute value.

Introduction

In the previous work [1], the critical behavior of the heat capacity of non-uniform liquid in a gravitational field and the shift of the temperature, which corresponds to a maximum of the heat capacity averaged over the altitude position, with respect to the critical temperature of the bulk homogeneous liquid were investigated. This work deals with the heat capacity features and the shift of the critical temperature, which arise owing to the spatial confinement of the liquid which is in the state near its critical point.

The behavior of non-uniform systems, embedded into external fields (in particular, the gravitational field of the Earth) and considered near to their critical points or their points of the phase transition of the second kind, is similar, to a great extent, to that of the confined systems, whose linear dimensions (single for a plane-parallel layer or several for cylindrical or spherical samples) become comparable, by the magnitude, with a correlation length of the order parameter fluctuations. This is caused by an entirely clear reason that the correlation length cannot exceed the linear dimensions of the confined system. Therefore, the interaction of the order parameter fluctuations, similarly to what happens in systems in external fields, cannot be abnormally large along the directions of the spatial confinement.

One of the interesting manifestations of the confinement of one-component liquids and liquid mixtures in the vicinity of their critical points is the shifts of their critical parameters (the critical temperature, density, and concentration) [2–4]. In connection to what was said above, such a shift is similar to a shift of the temperature which corresponds to a maximum of the heat capacity of the non-uniform liquid in a gravitational field, averaged over the altitude position, with respect to the critical temperature of the bulk phase of the homogeneous liquid in the absence of external fields, investigated in [1].

It is necessary to emphasize the significance of a theoretical research of such a kind in connection with experimental results of studying the influence of the system confinement on the specific heat of He^4 in the vicinity of its λ-point, which was carried out in [5–8]. As was marked in [7, 8], the research of the influence of gravitation on the specific heat of He^4 is of importance, because, according to the authors' opinion, there is a competition between two factors, the confinement of the sample and the dependence of the phase transition temperature on pressure, which results in the shift of the critical temperature. It was this obscure dependence of the shift of the temperature of the λ-transition in He^4 on the gravitation action that caused, in principle, the necessity of carrying out precise experimental researches of the specific heat of confined liquid helium in a plane-parallel gap 57 μm in thickness under the condition of space flight on board of the Space Shuttle from November 19 till December 4, 1997. The results of those researches of the critical behavior of the specific heat of confined liquid helium, provided the condition of microgravitation, were published in [7,8].

In the present work, we attempt to answer the question concerning the character of a competition between two effects, namely, the influence of gravitation and the system confinement on the system's critical temperature.

1. Heat Capacity of Confined Liquids

In accordance with the scaling hypothesis for confined systems, which was formulated for the first time in [2] (see also [4,9]), a singular part of the thermodynamic potential $\Delta\Phi_s$ of the one-component liquid, i.e. that of the Gibbs free energy ΔG_s for independent variables T, P or that of the Helmholtz free energy ΔF_s for independent variables T, V, depends not only on the temperature τ and an external field H but also on the linear dimensions of the system:

$$\Delta\Phi_s = L^{-d} f_\Phi(a\tau L^{1/\nu}, bHL^{\beta\delta/\nu}). \tag{1}$$

Therefore, the isochoric heat capacity of the confined liquid is characterized by the formula, which can be obtained by differentiating twice the singular part of the Helmholtz free energy with respect to the temperature, namely,

$$C_{vs} = \frac{\partial^2 \Delta\Phi_\mathrm{s}}{\partial\tau^2} = L^{-d+2/\nu} f_c(x,y), \tag{2}$$

where $f_c = a^2 f''_\Phi$, $-d + 2/\nu = \alpha/\nu$, and the scaling variables are $x = a\tau L^{1/\nu}$ and $y = bHL^{\beta\delta/\nu}$.

The scaling function $f_c(x,y)$ in Eq. (2) has the following asymptotics:

1. In a zero external field ($H = 0$, $y = 0$), the linear dimension of the bulk liquid considerably exceeds the correlation length of the density fluctuations ($L \gg \xi$). In this case, the scaling variable $x \sim [L/\xi(\tau)]^{1/\nu} \gg 1$ and the scaling function $f_c(x \gg 1, y = 0) \sim x^{-\alpha}$, which gives the well-known result $C_{vs} \sim \tau^{-\alpha}$ for the isochoric specific heat of the bulk liquid systems.

2. In the opposite case, where $L \ll \xi$, i.e. for the confined liquid in a zero external field, the scaling function $f_c(x \ll 1, y = 0) = \text{const}$ and the specific heat is characterized by the following dependence on the linear dimension: $C_{vs} \sim L^{\alpha/\nu}$.

3. In a nonzero external field at $x = 0$ and for the bulk liquid, the scaling variable $y \sim [L/\xi(\tau)]^{\beta\delta/\nu} \gg 1$. In this case, the scaling function $f_c(x = 0, y \gg 1) \sim x^{-\alpha/\beta\delta}$, which gives the well-known field dependence of the singular part of the isochoric specific heat of the bulk liquid: $C_{vs} \sim z^{-\alpha/\beta\delta}$.

4. In the confined liquid, which is in an external field at $x = 0$, the scaling function $f_c(x = 0, y \ll 1) = \text{const}$ and, consequently, $C_{vs} \sim L^{\alpha/\nu}$.

Consider now the critical temperature of the confined liquid. Analyzing an expression for the heat capacity

$$C_{vs} = \left(\frac{x}{a\tau}\right)^\alpha f_c(x,y), \tag{3}$$

which is totally equivalent to formula (2), one can make a conclusion that the confined liquid must be characterized by a new critical temperature $T_c^*(L)$, which depends on the linear size L of the system. It is the temperature, at which the heat capacity C_{vs} reaches its maximum value in the confined liquid.

The value of the new critical temperature $T_c^*(L)$ is determined from the condition of extremum of the heat capacity (3)

$$\frac{\partial C_{vs}}{\partial\tau} = -\alpha\left(\frac{x}{a\tau^*}\right)^{\alpha-1}\left(\frac{x}{a\tau^{*2}}\right) f_c + \left(\frac{x}{a\tau^*}\right)^\alpha f_c' a L^{1/\nu} = 0, \tag{4}$$

which gives

$$\tau^*(L) = \frac{\alpha f_c}{a f_c'} L^{1/\nu}. \tag{5}$$

for the shift $\tau^*(L) = [T_c^*(L) - T_c]/T_c$ of the critical temperature. It follows immediately from here that the shift of the new critical temperature $T_c^*(L)$ of the confined system with the linear dimension L is characterized with respect to that of the bulk one by a universal dependence on the system linear dimension, namely,

$$\tau^*(L) = [T_c^*(L) - T_c(\infty)]/T_c(\infty) \sim L^{-1/\nu}, \tag{6}$$

which is corroborated by experimental researches [5,8, 10,11].

At the same time, the factor $A_c = \alpha f_c / a f_c'$ in formula (5) has not any universal value. In principle, it has to vary for different properties of the confined liquid. Thus, as has already been noted in [4], the value of the new critical temperature T_c^* of the confined systems, at which a certain physical property (the order parameter, the susceptibility, the heat capacity, the correlation length, etc.) amounts to its maximum value, depends, generally speaking, on what property of the confined system is under consideration. For example, it follows from the condition of maximum of the susceptibility χ (for liquids, the isothermal compressibility β_T) or the correlation length ξ of the order parameter fluctuations that the role of the constant A_c in formula (5) is played by other quantities, $A_\chi = \gamma f_\chi / a f'_\chi$ or $A_\xi = \nu f_\nu / a f'_\nu$, where f_χ and f_ν are the scaling functions of the susceptibility and correlation length, respectively, of the confined system [9].

It should be noted that the nonuniversality of the shift amplitude of the new critical temperature in formula (5), owing to its dependence on a studied physical property, complicates very much the experimental researches, involved themselves, of the critical phenomena in confined systems. The problem "Is there, in general, any difference between the critical temperatures $T_c^*(L)$'s for different physical properties of confined systems?" is a problem which should be resolved first of all in experiment, because, in our opinion, the issue concerning the nonuniversality of the critical temperature shift in confined systems remains open for discussion in theoretical aspect.

Really, it is possible to suggest another theoretical approach for the definition of the new critical temperature $T_c^*(L)$ of confined systems (in particular, of one-component liquid), which uses known relations between various physical properties and the correlation length of the order parameter fluctuations in the critical region. For example, the isothermal compressibility of the liquid is connected to the correlation length of the density fluctuations by the following relation: $\beta_T \sim \xi^{2-\eta}$, where η is a critical exponent of the anomalous dimensionality of the pair correlation function G_2 of the order parameter fluctuations [12]. It is clear that if one use such relations and the formula for the correlation length in the confined system (see, e.g., [4,13])

$$\xi = L f_\xi (a\tau L^{1/\nu}, bHL^{\beta\delta/\nu}) \tag{7}$$

with the scaling function $f_\xi(x,y)$, which can be obtained in an explicit form for confined systems of various geometrical configurations with certain boundary conditions, the new critical temperature $T_c^*(L)$ will be determined only making use of the condition of extremum of the correlation length (7) and will not depend any more on other physical properties.

2. Influence of the Confinement and Gravitation on the Critical Temperature of He^4

For an estimation of the influence of the finite size on the specific heat of He^4, we shall use the known relation $C_{vs} \sim \xi^{\alpha/\nu}$ between the singular part of the heat capacity C_{vs} of the one-component liquid and the correlation length ξ of the density fluctuations, as well as the following formula, which was obtained in [9,14,15] for the correlation length of the density fluctuations in the liquid, the latter being near its critical point and confined to a narrow plane-parallel gap:

$$\xi = \xi_0 [\tau + (\pi/K)^{1/\nu}(1+\tau)]^{-\nu}. \tag{8}$$

Here, $K = d/\xi_0$ is a geometrical factor, which determines the width of the plane gap in terms of the correlation length amplitude ξ_0. For He^4, $\xi_0 = 0.36$ nm above and 0.14 nm below its λ-point [16], and the critical exponent $\nu = 0.6705$ [17].

The relation $C_{vs} \sim \xi^{\alpha/\nu}$ with formula (8) gives the following expression for the specific heat of the liquid in a flat gap:

$$C_{vs} \sim [\tau + (\pi/K)^{1/\nu}(1+\tau)]^{-\alpha}, \tag{9}$$

which enables an opportunity to estimate the temperature shift of the λ-transition in He^4 resulted from the confinement of the bulk, where the features of this phase transition of the second kind are studied.

The following data characterize the numerical experimental and theoretical values of the temperature shift $\Delta\tau_\lambda = (T_{\lambda b} - T_\lambda^*)/T_{\lambda b}$, where $T_{\lambda b} \approx 2.17$ K is the temperature of the λ-point of He^4 in the quasi-bulk state and T_λ^* is the temperature which corresponds to a maximum of the heat capacity of He^4 filling the flat gap: $(\Delta\tau_\lambda)_{\text{exp}} = 2.9 \times 10^{-8}$, $(\Delta\tau_\lambda)_{\text{theor}} = 2.3 \times 10^{-8}$. The theoretical value of the temperature shift of the λ-transition due to the finite size of the system was calculated according to formula (9), when approaching the λ-point from above. It turned out to be smaller by 20% than the experimental value [8], which should be adopted as rather a good result. The theoretical calculations also yielded the results which appeared very much close to those of the researches of the heat capacity of confined helium with the characteristic dimension of the gap within the interval of $0.107 - 0.692$ μm under terrestrial conditions [18].

The "exact" value of the λ-transition temperature $T_{\lambda b}$ in a large volume of He, necessary in the quoted calculations, was measured during the experiment [7], carried out on board of the Space Shuttle in October 1992. The optimum value of the critical exponent, which describes a divergence of the heat capacity below the transition point, was determined in this work to be −0.01285. The experimental value of the temperature shift of the λ-transition in confined He^4 was obtained in [8] with the use of the data concerning the specific heat capacity of helium, which filled a plane-parallel gap 57 μm in thickness under the conditions of the space zero-gravity and was at a temperature "distance" from the λ-point of no more than several nanokelvins, i.e. the nearest approach to the λ-transition temperature was achieved: $|T - T_{\lambda b}|_{\min} \approx 2 \times 10^{-9}$ K or $\tau_{\min} \approx 10^{-9}$. Such a high sensitivity with respect to the midget temperature changes was obtained due to the use of the perfect paramagnetic-salt thermometer [19] in the orbital experimental installation. This modern technique of measuring temperature, in the developers' opinion, will make it possible to investigate the confinement effect in rather big systems with characteristic dimensions of about 100 μm in the nearest future.

For an estimation of the influence of gravitation on the specific heat of He^4, consider first of all which limiting case, the vicinity of the critical isochore or the critical isotherm, was realized in [8]. For this purpose and taking into account the above-mentioned value $\tau_{\min} \approx 10^{-9}$, one has to compare the value of $(\tau_{\min})^{\beta\delta}$ with that of the dimensionless field variable in the theory of the gravitational effect $z = \rho_c g L/P_c$, where $L = 5.7 \times 10^{-5}$ m is the thickness of the plane gap, and $\rho_c = 0.145 \times 10^3$ kg/m^3 and $P_c \approx 5 \times 10^3$ Pa are the critical density and pressure, respectively, of He^4 near its λ-point. As a result, $(\tau_{\min})^{\beta\delta} \approx 10^{-15}$ and $z \approx 1.5 \times 10^{-5}$, i.e. the strong inequality $(\tau_{\min})^{\beta\delta} \ll z$ holds true, which is typical of the close vicinity of the critical isotherm.

Then, for an approximate estimation of the required shift of the temperature $T_\lambda$of the phase transitions of the second kinds in He^4, one may take advantage of formula (15) from [1]. Provided that all parameters in this formula remain untouched but the value of the critical temperature T_c, which should be substituted by $T_{\lambda b}$, one obtains ultimately that $(\Delta T_\lambda)^g_{\text{theor}} = T^*_\lambda - T_{\lambda b} \approx -5 \times 10^{-8}$ K or $(\Delta \tau_\lambda)^g_{\text{theor}} \approx -2.5 \times 10^{-8}$.

Thus, the theoretical estimations of the influence of the finite size of the system and gravitation on the shift of the critical temperature of He^4 give similar results by both the sign and the absolute value. The obtained result should be interpreted in such a manner that the value of the temperature shift of the λ-transition $(\Delta\tau_\lambda)_{\exp} = 2.9 \times 10^{-8}$, obtained experimentally under the conditions of microgravitaion in a space orbit [8], is caused entirely by the confinement of the system. On the other hand, in the laboratory environment on the Earth, one should expect the value of the temperature shift of the λ-transition in He^4 to be approximately twice as much by the absolute value, namely, $(\Delta\tau_\lambda)_{\exp} = 5.4 \times 10^{-8}$, because both the considered effects, the influence of gravitation and the system's finite size on the λ-transition temperature, cannot compensate but only strengthen each other.

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ТЕПЛОЄМНІСТЬ ТА ЗСУВ КРИТИЧНОЇ ТЕМПЕРАТУРИ В ПРОСТОРОВО ОБМЕЖЕНИХ РІДИНАХ

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Р е з ю м е

Отримано формулу для теплоємності просторово обмеженої однокомпонентної рідини в критичній області та знайдено нове значення критичної температури, яке відповідає максимуму теплоємності просторово обмеженої рідини. Одержані результати застосовано для вивчення впливу просторової обмеженості системи на питому теплоємність He^4 поблизу λ-точки і порівняно з результатами експерименту, який був проведений в умовах мікрогравітації під час космічного польоту на кораблі Space Shuttle у 1997 р. Розглянуто питання щодо існування конкуренції між двома ефектами — впливами на критичну температуру гравітації та просторової обмеженості системи. Теоретичні оцінки цих впливів на зсув температури λ-переходу в He^4 дають результати, однакові за знаком і близькі за абсолютною величиною.