
THERMAL DIFFUSIVITY, DIFFUSION, AND THERMODIFFUSION OF A SPATIALLY CONFINED BINARY LIQUID MIXTURE IN ITS CRITICAL REGION

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The features of the thermodiffusion phenomena in binary liquid mixtures spatially confined within small volumes of the cylindrical geometry have been studied near their liquid–vapor critical point. From this point of view, the formulae for the coefficients of thermal diffusivity and diffusion and the thermodiffusion relation which determine the width of the central component of the Rayleigh line have been obtained and analyzed. It has been shown that the thermodiffusion contribution to the generalized diffusion coefficient grows when removing from the critical point of a spatially confined binary mixture, contrary to the direct diffusion contribution behavior. The calculations proved that the value of the thermal diffusivity of a spatially confined system can considerably exceed the relevant value in a large volume. Naturally, the difference between the values of the thermal diffusivity in small and large volumes decreases with increase in the characteristic size of the system.

Studying the influence of the spatial confinement of a system on the critical behavior of the transport properties of a liquid represents the indisputable theoretical and experimental interest. First of all, it is connected to the large prevalence of the systems possessing the confined geometry in the nature. It is enough to recollect thin surface layers, interphases, pores, biomembranes, vesicles, synaptic fissures, and many other objects of physical, biological, and other origins as examples.

During some last decades, the phase transitions and the critical phenomena in spatially confined systems have been studied intensively on the basis of the scale invariance (the scaling hypothesis) and the renormalization-group approach ideas, numerical and real experiments (see, e.g., works [1–7]). One of the most promising methods for studying the complicated problem of the critical behavior of individual liquids

and liquid mixtures is the method of dynamical light scattering. This method allows the detailed information concerning the equilibrium and transport properties of a system to be obtained by analyzing the spectrum of the critical opalescence of light [8–17]. In particular, the width of the central component of the fine structure of the Rayleigh line contains data about such transport properties as the coefficients of diffusion, thermal diffusivity, and so on.

This work aims at studying the features of running the thermodiffusion phenomena in spatially confined binary liquid mixtures near their critical points. To put it more precisely, the work is devoted to obtaining the formulae for the coefficients of thermal diffusivity and diffusion and the thermodiffusion ratio which determine the width Γ_c of the central component of the Rayleigh line for a binary liquid mixture spatially confined within a small volume of cylindrical geometry, with the mixture being near its critical point “liquid–vapor”.

In the system with given geometry, the correlation length of order parameter fluctuations, which are the deviations of the total mixture density from its critical value $\varphi(\mu^*) = [\rho - \rho_c(\mu^*)] / \rho_c(\mu^*)$ (see the scaling hypothesis for spatially confined binary solutions [18]), looks like [19]

$$\xi = \xi_0 \left[\tau + (2\omega_1/K)^{1/\nu} (1 + \tau) \right]^{-\nu}, \quad (1)$$

where ξ_0 is the correlation length amplitude, $\omega_1 \approx 2.4048$ is the first zero point of the Bessel cylindrical function J_0 , $K = R/\xi_0$ is the geometrical factor that characterizes the number of monomolecular layers along the cylinder radius R , $\tau = (T - T_c)/T_c$ is the reduced deviation of the temperature from the critical value, and $\nu \approx 0.63$

is the critical index. Henceforth, the notation $\Psi_{\tau,K}$ is used for the expression $[\tau + (2\omega_1/K)^{1/\nu} (1 + \tau)]$ which defines the dependence of the properties of a spatially confined system on the temperature and size. One can easily see that the limit transition to the spatially unconfined system, $K \rightarrow \infty$, results in the dependence $\xi = \xi_0 \tau^{-\nu}$ for the correlation length in Eq. (1) which is a well-known result of the scaling theory of critical phenomena in a zero field (see, e.g., works [9–12]).

Below, we consider a single-phase region of the binary liquid mixture near its critical point of vaporization, where the external fields h_1 and h_2 , which were introduced in works [16, 17] and are the linear combination of the quantities $\Delta T = T - T_c$, $\Delta\mu_1 = \mu_1 - \mu_{1c}$, and $\Delta\mu = \mu - \mu_c$, satisfy the conditions $h_1 = 0$ and $h_2 = \tau = [T - T_c(\mu = \mu_c)]/T_c(\mu = \mu_c)$. Then, as was shown in works [16, 20], there are three temperature ranges, in which the critical behaviors of the transport coefficients and the corresponding dynamic properties (including the spectrum of the critical opalescence of light) of the binary liquid mixture are different, namely, (i) the range $\tau \gg \tau_1$, where the singular parts of the transport coefficients can be not taken into account; (ii) the range $\tau_D \ll \tau \ll \tau_1$, where the crossover from the regular to singular parts of the transport coefficients takes place; and (iii) the range $\tau \ll \tau_D$, where the singular parts of the transport coefficients substantially exceed their regular parts (it should be noted that, in most cases, the latter range is practically inaccessible in modern experiments).

The thermal diffusivity χ . As is known [21], the thermal diffusivity of a binary liquid mixture is defined by the formula $\chi = \lambda/\rho C_{P,x}$, where λ is the heat conductivity, ρ the total density of the mixture, and $C_{P,x}$ the isobaric heat capacity at a constant mixture content. At the critical point of the binary mixture, according to the results of works [10, 11, 22], the isobaric heat capacity, which is defined by the derivative $(\frac{\partial S}{\partial T})_{P,x}$, either is a constant (in the mean field theory or in the Landau thermodynamic theory of critical phenomena) or has a weak singularity $\sim \tau^{-\alpha}$ (in the scaling theory). Therefore, if one takes into account the point proved in works [23–25] that all peculiarities of the Onsager kinetic factors that enter the heat conductivity λ are totally compensated, the thermal diffusivity either becomes constant (in the mean field theory) or vanishes by the law $\chi \sim \tau^\alpha$ at $T \rightarrow T_c$ (in the scaling theory).

Making use of formula (1) for the correlation length results finally in the following expressions for the heat capacity $C_{P,x}$ and the thermal diffusivity χ in the liquid

mixture spatially confined within a small volume of cylindrical geometry:

$$C_{P,x} = C_{P,x}^0 (\xi/\xi_0)^{\alpha/\nu} = C_{P,x}^0 \Psi_{\tau,K}^{-\alpha}, \quad (2)$$

$$\chi = \chi_0 (\xi/\xi_0)^{-\alpha/\nu} = \chi_0 \Psi_{\tau,K}^{\alpha}, \quad (3)$$

where $C_{P,x}^0$ and $\chi_0 = \lambda/\rho C_{P,x}^0$ are the peak value of the isobaric heat capacity at a constant mixture composition and the amplitude of the heat conductivity, respectively. From formulae (2) and (3), one can see that the extreme values of the heat capacity and the thermal diffusivity of the spatially confined binary mixture are not reached at $\tau = 0$, i.e. at the critical temperature of the bulk phase T_c , but at a lower temperature T^* which is defined by the condition

$$\tau^* = (T^* - T_c)/T_c = -[1 + (K/2\omega_1)^{1/\nu}]^{-1}. \quad (4)$$

Diffusion and thermal diffusion. Consider now the critical behavior of the quantity

$$\Delta = D \left[1 + \frac{k_T^2}{TC_{P,x}} (\partial\mu/\partial x)_{P,T} \right] = \Delta_1 + \Delta_2, \quad (5)$$

which, as was shown in works [26, 27], characterizes the joint contribution of the diffusion (the first term on the right-hand side which corresponds to Fick's law) and the thermal diffusion (the second term which corresponds to the Soret effect) to the width Γ_c of the central component of the Rayleigh line. The direct diffusion effect Δ_1 is described by the coefficient of mass diffusion D ($\Delta_1 = D$). Its peculiar behavior at the critical point of the spatially confined mixture is characterized by the following formula which stems from the Stokes–Einstein relation:

$$D = D_0 (\xi/\xi_0)^{-1} = D_0 \Psi_{\tau,K}^{\nu}, \quad (6)$$

where $D_0 = kT/6\pi\eta\xi_0$ is the amplitude of the diffusion coefficient. We note that formula (6) is valid in the temperature range $\tau \ll \tau_D$, where the singular parts of the transport coefficients exceed their regular parts considerably.

Within the range $\tau_D \ll \tau \ll \tau_1$, which is observed experimentally and where the regular parts of the transport coefficients should be taken into account together with their singular parts, the following scaling formula for the diffusion coefficient takes place:

$$D = D_0 \Psi_{\tau,K}^{\gamma}. \quad (7)$$

While obtaining this formula, the corresponding result of work [16] for a spatially unconfined binary mixture was used.

It is natural that, in the temperature range $\tau \gg \tau_1$, where the singular parts of the transport coefficients are not necessary to be taken into account, the diffusion coefficient D ceases to depend on how close the thermodynamic parameters of the system are to their critical values and acquires an almost constant value which is not the function of τ .

Concerning the second term in formula (5), $\Delta_2 = \Delta - D = \Delta - \Delta_1 = D \frac{k_T^2}{TC_{P,x}} (\partial\mu/\partial x)_{p,T}$ which defines the contribution of the thermal diffusion, the thermodiffusion ratio k_T diverges proportionally to the correlation length in the range $\tau \ll \tau_D$, i.e.

$$k_T = k_{T0} (\xi/\xi_0) = k_{T0} \Psi_{\tau,K}^{-\nu}. \quad (8)$$

In the crossover range $\tau_D \ll \tau \ll \tau_1$, the divergence of k_T becomes stronger:

$$k_T = k_{T0} (\xi/\xi_0) = k_{T0} \Psi_{\tau,K}^{-\gamma}. \quad (9)$$

Furthermore, as the susceptibility of the binary mixture $(\partial x/\partial\mu)_{P,T}$ possesses a strong singularity, the reciprocal value of this derivative, which enters the thermodiffusion term Δ_2 , behaves as a “strong zero” according to the formula

$$(\partial\mu/\partial x)_{P,T} = (\partial\mu/\partial x)_{P,T}^0 \Psi_{\tau,K}^{\gamma}, \quad (10)$$

and the isobaric heat capacity at a constant mixture composition $C_{P,x}$, as was emphasized above, is determined by formula (2).

In accordance with that, the thermodiffusion contribution Δ_2 to the generalized diffusion coefficient Δ behaves as follows when approaching the critical point of the spatially confined binary liquid mixture:

(i) In the temperature range $\tau \ll \tau_D$, where the singular parts of the transport coefficients substantially exceed their regular parts, we have

$$\Delta_2 = \Delta_{20} \Psi_{\tau,K}^{\alpha-\nu(1-\eta)} \quad (11)$$

where $\Delta_{20} = D_0 k_{T0} (\partial\mu/\partial x)_{P,x}^0 / TC_{P,x}^0$ is the amplitude which, naturally, has no singularity at the critical point. When obtaining formula (11), we used the scaling identity $\gamma = (2-\eta)\nu$. Taking into account the numerical values of the critical indices $\alpha \approx 0.11$, $\gamma \approx 1.24$, $\nu \approx 0.63$, and $\eta \approx 0.03$ [10, 11, 28–30], we have $\alpha + \nu(1-\eta) \approx 0.72$ for the power exponent in Eq. (11). Therefore, in the asymptotic range $\tau \ll \tau_D$, where

the scaling laws for the transport coefficients operate, we have $\Delta \approx \Delta_1 + \Delta_2 \sim \tau^\nu + \tau^{\alpha+\nu(1-\eta)} \sim \tau^{0.63} + \tau^{0.72}$ for the mutual contribution of the diffusion and thermal diffusion effects. Then, the ratio $\Delta_2/\Delta_1 \sim \tau^{0.09}$ tends to zero in the asymptotically close vicinity of the critical point, where $\tau \rightarrow 0$. This means that one may practically neglect the thermodiffusion contribution Δ_2 in comparison with the direct diffusion effect (the mass diffusion coefficient) $\Delta_1 = D$.

(ii) In the temperature range $\tau_D \ll \tau \ll \tau_1$, where the crossover from the regular to singular parts of the transport coefficients takes place, the thermodiffusion contribution

$$\Delta_2 = \Delta_{20} \Psi_{\tau,K}^{\alpha} \quad (12)$$

behaves as a “weak zero”.

Thus, in the experimentally achievable range of temperatures $\tau_D \ll \tau \ll \tau_1$, the generalized diffusion coefficient of the spatially confined binary liquid mixture behaves according to the formula

$$\Delta \approx \Delta_1 + \Delta_2 \sim \tau^\gamma + \tau^\alpha \sim \tau^{1.24} + \tau^{0.11}. \quad (13)$$

Since $\gamma \gg \alpha$, it is the thermal diffusion that plays the principal role in this temperature interval, i.e. $\Delta \approx \Delta_2$, and whose temperature dependence in the spatially confined mixture is given by formula (12).

One should pay attention to a change of the ratio Δ_2/Δ_1 when passing from the asymptotic range $\tau \ll \tau_D$, which is practically unattainable under experimental conditions, to the crossover range $\tau_D \ll \tau \ll \tau_1$ which can be observed experimentally. In the former range, as was indicated above, the ratio $\Delta_2/\Delta_1 \ll 1$ with $\Delta_2/\Delta_1 \rightarrow 0$ when approaching the critical point. On the contrary, in the latter one, the inverse inequality $\Delta_2/\Delta_1 \gg 1$ takes place. The physical meaning of the sign change in those inequalities consists in the enhancement of the thermodiffusion contribution, when moving apart from the critical point of the spatially confined binary mixture in comparison with the mere diffusion one. The inequality $\Delta_2/\Delta_1 \gg 1$ was confirmed by theoretical calculations [17] when analyzing the experimental data on dynamic scattering of light [15] in a binary mixture methane–ethane which occupied a large volume. For example, provided the temperature deviation $T - T_c = 0.1$ K and the ethane concentration $x = 0.2893$, the ratio $\Delta_2/\Delta_1 = \frac{k_T^2}{TC_{P,x}} (\partial\mu/\partial x)_{P,T}$ was about 50.

All the stated above concerning the peculiarities of the critical behavior of the thermal diffusivity and the isobaric heat capacity at a constant mixture

composition remains in force with respect to the critical behavior of all the diffusion and thermodiffusion contributions. Namely, their extreme values in the spatially confined binary mixture are not reached at the critical temperature of the bulk phase T_c ($\tau = 0$), but at a definite temperature deviation τ^* , which is determined by formula (4).

There are two important remarks concerning the use of theoretical and experimental data on the heat capacity, susceptibility, coefficients of diffusion and heat conductivity, and other similar equilibrium and transport properties of spatially confined and unconfined binary liquid mixtures.

1. Let some quantity $A(x)$ regular in the critical range and dependent on the mixture concentration be given, as well as its known experimental (or theoretical) value $A(x_0)$ at a fixed concentration x_0 . If so, the values of this quantity $A(x)$ at a small or, in a linear approximation, any concentration of the mixture can be determined by the relationship [17]

$$A(x) \approx A(x_0) \frac{x}{x_0}. \quad (14)$$

But if the researched quantity does depend on the concentration in a singular manner, i.e. $A(x) \sim x^m$, relationship (14) acquires the form

$$A(x) \approx A(x_0) \left[\frac{x}{x_0} \right]^m. \quad (15)$$

2. In the same manner, one can obtain a relationship between the value $A(K)$ of an arbitrary quantity in a spatially confined individual liquid or a binary liquid mixture and the value $A(\infty)$ of this quantity in the relevant unconfined system in terms of the corresponding dependences $A(K)$ and $A(\infty)$ on the correlation lengths $\xi(K)$ and $\xi(\infty)$, i.e. $A(K) \sim [\xi(K)]^n$, $A(\infty) \sim [\xi(\infty)]^n$. The required relationship between $A(K)$ and $A(\infty)$ looks like

$$A(K) \approx A(\infty) \left[\frac{\xi(K)}{\xi(\infty)} \right]^n. \quad (16)$$

Therefore, according to formulae (14)–(16), any quantity $A(K, x)$ at any mixture concentration in a small volume that is characterized by the geometrical factor K can be evaluated as

$$A(K, x) \approx A(\infty, x_0) \left[\frac{x}{x_0} \right]^m \left[\frac{\xi(K)}{\xi(\infty)} \right]^n \quad (17)$$

if one knows the experimental (theoretical) value of this quantity at a certain concentration in the spatially unconfined binary liquid mixture.

As an example of applying the proposed method for calculating the physical properties of the spatially confined binary liquid mixture, let us consider the thermal diffusivity $\chi = \lambda/\rho C_{P,x}$ of the mixture with a fixed composition (ethane 71.07% and methane 28.93%) in a small volume of cylindrical geometry. We recall that the critical behavior of the thermal diffusivity coefficient is governed by the weak divergence of the isobaric heat capacity at a constant composition. Then, on the basis of formulae (6) and (16), the thermal diffusivity coefficient reads

$$\frac{\chi(K)}{\chi(\infty)} = \left(\frac{\Psi_{\tau,K}}{\tau} \right)^\alpha. \quad (18)$$

Experimental results [14, 15] and theoretical calculations [16, 17] reveal that the thermal diffusivity of the considered mixture at $T - T_c = 0.1$ K and in a practically unconfined volume is equal to $8 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. The absolute temperature deviation $T - T_c = 0.1$ K corresponds to the dimensionless temperature variable $\tau = (T - T_c)/T_c = 0.447 \times 10^{-3}$, because the critical temperature of the methane–ethane mixture of the given composition, taking the values of the critical temperatures of the pure components into account, $T_c^{(m)} = 190.564$ K for methane and $T_c^{(e)} = 305.322$ K for ethane, is equal to $T_c = T_c^{(m)}(1 - x) + T_c^{(e)}x = 223.764$ K. As a result, adopting the critical index $\alpha \approx 0.11$ and the geometrical factor $K = 10^2$, we obtain $\chi(K) \approx 1.2 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. It is the value of the thermal diffusivity of the spatially confined system $\chi(K)$, which is approximately half as much again as $\chi(\infty)$. It is explained by the fact that the extremum of the thermal diffusivity $\chi(\infty)$ in a large volume is achieved at $\tau = 0$, whereas it is realized for the quantity $\chi(K)$ in the temperature range below T_c . As a result, $\chi(\infty) < \chi(K)$ at any fixed temperature above T_c . Naturally, the difference between the values of the thermal diffusivity in small and large volumes decreases with increase in the geometrical factor K . For example, if the geometrical factor grows by an order of magnitude, i.e. $K_1 = 10^3$, the thermal diffusivity $\chi(K_1) \approx 8.6 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. That is, the relative difference of the temperature conductivities in small and large volumes decreases to the value $[\chi(K_1) - \chi(\infty)]/\chi(\infty) \approx 7.5\%$.

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ТЕМПЕРАТУРОПРОВІДНІСТЬ, ДИФУЗІЯ
І ТЕРМОДИФУЗІЯ ПРОСТОРОВО ОБМЕЖЕНОЇ
БІНАРНОЇ РІДКОЇ СУМІШІ В КРИТИЧНІЙ ОБЛАСТІ

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Резюме

Вивчено особливості протікання термодифузійних явищ в просторово обмежених бінарних рідких сумішах, що перебувають у малому об'ємі циліндричної геометрії поблизу критичної точки рідина—пара. У визначеному контексті отримано і проаналізовано формули для коефіцієнтів температуропровідності, дифузії і термодифузійного відношення, які визначають ширину центральної компоненти лінії Релея. Показано, що термодифузійний внесок в узагальнений коефіцієнт дифузії зростає в порівнянні з прямим дифузійним внеском з віддаленням від критичної точки просторово обмеженої бінарної суміші. Проведені розрахунки довели, що значення температуропровідності просторово обмеженої системи може значно перевищувати температуропровідність у великому об'ємі. Із збільшенням характерного розміру системи різниця між значеннями температуропровідності в малому і великому об'ємах природно, зменшується.