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Transport Properties of Critical Dilute Solutions

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On the basis of the isomorphism of critical phenomena, the behavior of transport properties of binary mixtures in the vicinity of the vapor–liquid critical line is considered. In particular, the renormalization of the singularity of the thermal conductivity in dilute critical solutions has been analyzed in detail. It is shown that the behavior of the thermal conductivity is determined by the "critical background," i.e., the fluctuation-induced regular part, which diverges at the critical point of a solvent.

KEY WORDS: critical line; critical phenomena; dilute solutions; thermal conductivity; transport properties; vapor–liquid.

1. INTRODUCTION

It is well-known that in the vicinity of the vapor–liquid critical point of a fluid, both thermodynamic and transport properties manifest singular power-law behavior (see, for example, Refs., 1 and 2). The exponents of these power laws (critical exponents) are universal, i.e., system indepenent. The hypothesis of isomorphism of critical phenomena allows one to generalize the concept of universality, formulated at first for one-component fluids, to binary and multicomponent mixtures [3, 4]. Near-critical systems will be isomorphic if the corresponding free energies have the same functional dependences on the thermodynamic variables provided that they are suitably chosen. A rule for the choice of isomorphic variables is determined by the stability-limit condition of a system with respect to variations of the order parameter.

At the critical point of a binary mixture the stability-limit condition is

$$\left(\frac{\partial^2 \rho A^*}{\partial \rho^2}\right)_{T,\mu} = \frac{1}{\rho}\left(\frac{\partial P}{\partial \rho}\right)_{T,\mu} = 0 \tag{1}$$

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where the density of the "isomorphic" free energy ρA^* and the pressure P depend on the temperature T, density ρ, and field variable μ, which is equal to the difference of the chemical potentials of the two components, $\mu = \mu_2 - \mu_1$. The isomorphic variable μ is conjugate to the mole fraction of the second component

$$x = N_2/(N_1 + N_2) = -\left(\frac{\partial A^*}{\partial \mu}\right)_{T,\rho} \tag{2}$$

where N_1 and N_2 are the number of moles of the components. The isomorphic molar free energy A^* is connected with the Helmholtz molar free energy A of a mixture by the relation

$$A^*(T, v, \mu) = A(T, v, x) - \mu x \tag{3}$$

where $v = 1/\rho$ is the molar volume. As $x \to 0$ and as $x \to 1$ the critical line terminates at the critical points of the pure components, while the free energy $A^*(T, v, \mu)$ approaches the usual Helmholtz free energy $A(T, v)$. The isomorphism hypothesis assumes that, at the constant field variable μ, the free-energy density ρA^* has the identical functional dependence on temperature and order parameter that ρA has in a one-component fluid. In other words, if the temperature distance to the critical point of a mixture

$$\tau(\mu) = \frac{T - T_c(\mu)}{T_c(\mu)}$$

and the order parameter

$$\varphi(\mu) = \frac{\rho - \rho_c(\mu)}{\rho_c(\mu)}$$

are, respectively, the dimensionless deviation of temperature and density from their critical values $T_c(\mu)$ and $\rho_c(\mu)$, and the singular part of ρA^* depends on $\tau(\mu)$ and $\varphi(\mu)$ at $\mu = \text{constant}$ just the same as the singular part of ρA in a one-component fluid depends on $\tau = (T - T_c)/T_c$ and on the order parameter $\varphi = (\rho - \rho_c)/\rho_c$. In the scaling theory [5, 6]

$$\rho A^* = |\tau(\mu)|^{2-\alpha}\, \Psi(z) + \rho A_0^* \tag{4}$$

where $z = |\varphi(\mu)|^{1/\beta}/\tau(\mu)$, $\Psi(z)$ is a universal function, while ρA_0^* is a regular background. Thus in binary mistures, one can introduce the thermodynamic properties which manifest the universal asymptotic critical power laws. For example, in the one-phase region $(\tau(\mu) > 0)$ at the critical isochore $[\rho = \rho_c(\mu)]$, the singular parts of the isomorphic specific heats and susceptibility read

$$C_{V,\mu}/R = A_0 \tau^{-\alpha}(\mu) \tag{5}$$

$$RT_{c0}\left(\frac{\partial \rho}{\partial P}\right)_{T,\mu} = \Gamma_0 \tau^{-\gamma}(\mu) \tag{6}$$

$$C_{P,\mu}/R = \Gamma_0 (T_c/P_c)^2 \, (dP_c/dT_c)^2 \, \tau^{-\gamma}(\mu) \tag{7}$$

where R is the gas constant, T_{c0} is the critical temperature of the solvent, P_c is the critical pressure of the mixture, the derivative (dP_c/dT_c) is taken along the critical line, A_0 and Γ_0 are the system-dependent critical amplitudes, and α and γ are universal critical exponents. Just as in one-component fluids, the correlation length of the critical fluctuations of the order parameter diverges at the critical points of mixtures:

$$\xi = \xi_0 \tau^{-\nu}(\mu) \tag{8}$$

where ξ_0 is the bare correlation length, of the order of a molecular size. According to the latest renormalization-group calculations (see Ref. 2 and references cited therein), $\alpha = 0.110 \pm 0.003$, $\gamma = 1.239 \pm 0.002$, $\nu = \gamma/(2-\eta) = 0.630 \pm 0.001$, and $\eta = 0.031 \pm 0.001$. The theoretical values of the critical exponent are in excellent agreement with numerous experimental studies (for reviews see Refs. 7 and 8).

The purpose of this paper is to consider the behavior of thermodynamic and transport properties in binary mixtures on the basis of the concept of the universality of critical phenomena. In Section 2, the renormalization of the thermodynamic properties of binary mixtures is analyzed and simple expressions for the crossover from one-component-like behavior to mixture-like behavior are proposed. In Section 3, the crossover equations are applied to the dilute-solution case for which the explicit dependence on concentration can be derived. Section 4 contains the analysis of transport properties in critical mixtures. It is shown that the cross terms between singular and background parts of the transport properties determine the character of renormalization of the thermal conductivity in mixtures. Finally, the explicit form of the concentration dependence of the transport properties is presented for critical dilute solutions in Section 5.

2. RENORMALIZATION OF THE THERMODYNAMIC PROPERTIES

Experimental conditions may impose restrictions on the choice of thermodynamic variables. It is, in practice, impossible to maintain the condition $\mu = \text{constant}$ while the temperature varies (to do this, the composition would have to be varied during the measurements). Experiments are therefore usually performed at constant ρ and x, while μ is a function of temperature. In this case the experimental conditions are not isomorphic, and the universal power laws inherent in one-component fluids are not observed. The connection between the isomorphic path $t(\mu)$ and the experimental path $\tau(x)$ is not analytic [8],

$$\tau^{1-\alpha}(\mu)[1+\tau^{\alpha}(\mu)\, y_2/X_A] = \tau(x)\, y_1/X_A \tag{9}$$

where the parameter

$$X_A = \frac{A_0 R T_c}{(1-\alpha)} \frac{dx}{d\mu_c} \left(\frac{1}{T_c}\frac{dT_c}{dx}\right)^2 \tag{10}$$

is equal to zero at the critical points of the pure components, and the system-dependent parameters y_1 and y_2 are of the order of unity and equal to unity in the pure-component limit. Far away from the critical point, when

$$\tau(x) \gg X_A^{1/\alpha} \tag{11}$$

$$\tau(\mu) \simeq \tau(x) \tag{12}$$

and all the isomorphic properties at $x = \text{constant}$ behave as those in one-component fluids [Eqs. (5)–(8)]. Asymptotically close to the critical point, when

$$\tau(x) \ll X_A^{1/\alpha} \tag{13}$$

$$\tau(\mu) = [(\tau(x)/X_A]^{1/(1-\alpha)} \tag{14}$$

and renormalization of critical exponents (the "Fisher renormalization") takes place (see, for example, Refs. 3 and 8),

$$C_{V,\mu} = A_0 R[\tau(x)/X_A]^{-\alpha/(1-\alpha)} + (C_{V,\mu})_b \tag{15}$$

where $(C_{V,\mu})_b$ is a "background" specific heat,

$$\mathrm{RT}_{c0}\left(\frac{\partial\rho}{\partial P}\right)_{T,\mu} = \Gamma_0[\tau(x)/X_A]^{-\gamma/(1-\alpha)} \tag{16}$$

$$\xi = \xi_0[\tau(x)/X_A]^{-\nu/(1-\alpha)} \tag{17}$$

Equation (9) determines the crossover between one-component-like behavior and renormalized behavior of the isomorphic properties. The behavior of the nonisomorphic properties (derivatives of the Helmholtz free energy at $x = \text{constant}$) appear to be more sophisticated. The isochoric specific heat $C_{V,x}$ at constant x behaves similar to that in a one-component fluid and similar to the isomorphic specific heat $C_{V,\mu}$ [Eq. (5)] in the region determined by inequality (11). However, asymptotically close to the critical point, at the condition of inequality (13), the specific heat $C_{V,x}$ does not diverge any more, remaining finite at the critical point. It is a cusp with the infinite derivative [8]:

$$C_{V,x} = R(A_0/X_{\mathrm{A}})(1 - X_{\mathrm{A}}^{-1}[\tau(x)/X_{\mathrm{A}}]^{\alpha/(1-\alpha)}) + (C_{V,x})_{\mathrm{b}} \tag{18}$$

Note that the value of $C_{V,x}$ at the critical point ("critical background")

$$(C_{V,x})_{\mathrm{cb}} = R\frac{A_0}{X_{\mathrm{A}}} \tag{19}$$

is not equal to its regular part $(C_{V,x})_{\mathrm{b}}$ and contains the critical amplitude A_0. The derivative $(\partial P/\partial \rho)_{T,x}$ may be written in the form

$$\left(\frac{\partial P}{\partial \rho}\right)_{T,x} = \left(\frac{\partial P}{\partial \rho}\right)_{T,\mu} + \rho^2 \left(\frac{\partial \mu}{\partial x}\right)_{\rho,T} \left(\frac{\partial x}{\partial \rho}\right)^2_{T,\mu} \tag{20}$$

With account of Eqs. (2), (4), and (6) we have

$$\left(\frac{\partial \mu}{\partial x}\right)_{\rho,T} \simeq \frac{d\mu_{\mathrm{c}}}{dx}[X_{\mathrm{A}}\tau^{-\alpha}(\mu) + 1]^{-1} \tag{21}$$

where the derivative $d\mu_{\mathrm{c}}/dx$ taken along the critical line is constant "in general." Then Eq. (20) at the critical isohore $\rho = \rho_{\mathrm{c}}(\mu)$ takes the form

$$\left(\frac{\partial P}{\partial \rho}\right)_{T,x} = \frac{RT_{\mathrm{c}0}}{\Gamma_0}\tau^{\gamma}(\mu)\left[1 + \frac{X_{\Gamma}\tau^{-\gamma}(\mu)}{X_{\mathrm{A}}\tau^{-\alpha}(\mu) + 1}\right] \tag{22}$$

where the new characteristic parameter X_{Γ} reads [8]

$$X_{\Gamma} = \frac{\Gamma_0}{y_2}\frac{dx}{d\mu_{\mathrm{c}}}\frac{T_{\mathrm{c}}}{RT^2_{\mathrm{c}0}\rho^2_{\mathrm{c}0}}\left[\frac{dP_{\mathrm{c}}}{dx} - \left(\frac{\partial P}{\partial T}\right)_{\substack{\mu_c,\,\rho_c\\(T=T_c)}}\frac{dT_{\mathrm{c}}}{dx}\right]^2 \tag{23}$$

The expression in brackets in Eq. (23) is proportional to the derivative $(\partial P/\partial x)_{T,\mathrm{coex}}$ taken at the condition of two-phase coexistence. This derivative is zero in an azeotropic mixture. In general, this derivative is not zero. Since $\gamma \simeq 1$, the range of the renormalization of the susceptibility is not very sensitive to the precise value of X_{Γ}. Below we put this value equal to (dP_c/dx). Thus the properties associated with a strong singularity in one-component fluids, such as the isothermal compressibility and isobaric specific heat at constant x, manifest in binary mixtures the crossover from the strong singularity to the weak one. Their crossover behavior is determined by two similar, but numerically not equal, characteristic parameters, X_Γ and X_A, introduced above. Far away from the critical point, when

$$\tau(x) \gg X_\Gamma^{1/\gamma} \tag{24}$$

$C_{P,x}$ and $(\partial\rho/\partial P)_{T,x}$ behave as C_P and $(\partial\rho/\partial P)_T$ in one-component fluids and as $C_{P,\mu}$ and $(\partial\rho/\partial P)_{T,\mu}$ in binary mixtures [Eqs. (6) and (7)]. Asymptotically close to the critical point [at the condition given by Eq. (13)], $C_{P,x}$ and $(\partial\rho/\partial P)_{T,x}$ manifest the weak singularity with the renormalized critical exponent α:

$$C_{P,x} = A_0 R[\tau(x)/X_\mathrm{A}]^{-\alpha/(1-\alpha)} \tag{25}$$

$$\left(\frac{\partial\rho}{\partial P}\right)_{T,x} = \Gamma_0 \frac{X_\mathrm{A}}{X_\Gamma}[\tau(x)/X_\mathrm{A}]^{-\alpha/(1-\alpha)} \tag{26}$$

At last, in the range of temperatures

$$X_\mathrm{A}^{1/\alpha} \leqslant \tau(x) \leqslant X_\Gamma^{1/\gamma} \tag{27}$$

$C_{P,x}$ and $(\partial\rho/\partial P)_{T,x}$ demonstrate the crossover from one-component-like behavior to renormalized behavior.

The special consideration needs to be made of properties that are characteristic of binary mixtures and that do not exist in one-component fluids. The "osmotic compressibility,"

$$\begin{aligned}\left(\frac{\partial x}{\partial\mu}\right)_{P,T} &= \left(\frac{\partial x}{\partial\mu}\right)_{\rho,T}\left(\frac{\partial P}{\partial\rho}\right)_{T,x}\left(\frac{\partial\rho}{\partial P}\right)_{T,\mu}\\ &= \frac{dx}{d\mu_\mathrm{c}}\left\{X_\Gamma\left[\frac{\tau(x)}{(X_\mathrm{A}+\tau^\alpha(x))}\right]^{-\gamma/(1-\alpha)}+1\right\}\end{aligned} \tag{28}$$

has a strong singularity, as $(\partial\rho/\partial P)_{T,\mu}$, only when $\tau(x) \ll X_\Gamma^{1/\gamma}$. In this range this property can be regarded as the critical susceptibility just as $(\partial\rho/\partial P)_{T,\mu}$. Far away from the critical point $(\tau(x) \gg X_\Gamma^{1/\gamma})$ the derivative $(\partial x/\partial\mu)_{P,T}$ is regular since the product $(\partial P/\partial\rho)_{T,x}\,(\partial\rho/\partial P)_{T,\mu}$ is constant in this region. Asymptotically close to the critical point $(\tau(x) \ll X_\mathrm{A}^{1/\alpha})$

$$\left(\frac{\partial x}{\partial\mu}\right)_{\rho,T} \sim \left(\frac{\partial\rho}{\partial P}\right)_{T,x} \sim [\tau(x)/X_\mathrm{A}]^{-\alpha/(1-\alpha)} \tag{29}$$

and

$$\left(\frac{\partial x}{\partial \mu}\right)_{P,T} \sim \left(\frac{\partial \rho}{\partial P}\right)_{T,\mu} \sim [\tau(x)/X_{\mathrm{A}}]^{-\gamma/(1-\alpha)} \tag{30}$$

In the region $X_{\mathrm{A}}^{1/\alpha} \leqslant \tau(x) \leqslant X_{\Gamma}^{1/\gamma}$ both derivatives, $(\partial x/\partial \mu)_{P,T}$ and $(\partial x/\partial \mu)_{\rho,T}$, exhibit crossover from regular mixture-like behavior to the singular critical behavior: "strong" for $(\partial x/\partial \mu)_{P,T}$ and "weak" for $(\partial x/\partial \mu)_{\rho,T}$.

3. CROSSOVER IN DILUTE SOLUTIONS

A dilute solution ($x \ll 1$) provides a good opportunity to demonstrate explicitly the crossover from one-component-like critical behavior of the thermodynamic properties to mixture-like behavior as a function of the solute concentration.

In a dilute solution along the critical line

$$x = -\frac{\partial A^*}{\partial \mu} = \exp\left(\frac{\mu_{\mathrm{c}}}{RT_{\mathrm{c}}}\right) \tag{31}$$

where μ_{c} is the critical value of μ. Thus we have

$$\frac{dx}{d\mu_{\mathrm{c}}} = \frac{x}{RT_{\mathrm{c}}} \tag{32}$$

$$\frac{dT_{\mathrm{c}}}{d\mu_{\mathrm{c}}} = \frac{dT_{\mathrm{c}}}{dx}\frac{x}{RT_{\mathrm{c}}} \tag{33}$$

In addition, we assume that

$$\left(\frac{\partial P}{\partial x}\right)_{T,\mathrm{coex}} \simeq \frac{dP_{\mathrm{c}}}{dx} \tag{34}$$

In the parameters X_{A} and X_{Γ} that determine the renormalization of the thermodynamic properties, the small parameter x appears:

$$X_{\mathrm{A}} \simeq A_0 x \left(\frac{1}{T_{\mathrm{c}}}\frac{dT_{\mathrm{c}}}{dx}\right)^2 \tag{35}$$

$$X_{\Gamma} \simeq \Gamma_0 x \left(\frac{1}{P_{\mathrm{c}}}\frac{dP_{\mathrm{c}}}{dx}\right)^2 \tag{36}$$

Thus the behavior of a critical dilute solution is determined by two "cones": a wide one, $\tau \sim X_{\Gamma}^{1/\gamma}$, and a narrow one, $\tau \sim X_{\mathrm{A}}^{1/\alpha}$. Strong singularities $(\partial \rho/\partial P)_{T,x} \sim C_{P,x} \sim \tau^{-\gamma}$ are cut off within the wide cone, while within the narrow cone the Fisher renormalization of the critical exponents takes place. Let us consider, for example, the quantity $(\partial\mu/\partial x)_{P,T}$, characterizing the thermodynamic stability of a binary mixture [see Eq. (28)]. At $\tau \gg X_{\Gamma}^{1/\gamma}$

$$\left(\frac{\partial\mu}{\partial x}\right)_{\rho,T} = \frac{RT}{x} \tag{37}$$

$$\left(\frac{\partial\rho}{\partial P}\right)_{T,x}\left(\frac{\partial P}{\partial\rho}\right)_{T,\mu} \simeq 1 \tag{38}$$

and

$$\left(\frac{\partial\mu}{\partial x}\right)_{P,T} \simeq \frac{RT}{x} \tag{39}$$

In the range $X_{\mathrm{A}}^{1/\alpha} < \tau < X_{\Gamma}^{1/\gamma}$

$$\left(\frac{\partial\mu}{\partial x}\right)_{\rho,T} = \frac{RT}{x} \tag{40}$$

$$\left(\frac{\partial P}{\partial\rho}\right)_{T,x} \simeq RT_{\mathrm{c}0}\Gamma_0^{-1}X_\Gamma \simeq RT_{\mathrm{c}0}x\left(\frac{1}{P_{\mathrm{c}}}\frac{dP_{\mathrm{c}}}{dx}\right)^2 \tag{41}$$

$$\left(\frac{\partial P}{\partial\rho}\right)_{T,\mu} = RT_{\mathrm{c}0}\Gamma_0^{-1}t^{\gamma}(x) \tag{42}$$

and, as it follows from Eq. (28),

$$\left(\frac{\partial\mu}{\partial x}\right)_{P,T} = \frac{RT}{x^2\Gamma_{\mathrm{c}}}\left(\frac{1}{P_{\mathrm{c}}}\frac{dP_{\mathrm{c}}}{dx}\right)^{-2}\tau^{\gamma}(x) \tag{43}$$

which is zero at all points on the critical line.[2] Finally, in the range $\tau \ll X_{\mathrm{A}}^{1/\alpha}$ asymptotically close to the critical point

$$\left(\frac{\partial\mu}{\partial x}\right)_{\rho,T} = \frac{RT}{xX_{\mathrm{A}}}\left(\frac{\tau(x)}{X_{\mathrm{A}}}\right)^{\alpha/(1-\alpha)} \tag{44}$$

$$\left(\frac{\partial P}{\partial\rho}\right)_{T,x} = RT_{\mathrm{c}0}\Gamma_0^{-1}\left(\frac{X_\Gamma}{X_{\mathrm{A}}}\right)\left(\frac{\tau(x)}{X_{\mathrm{A}}}\right)^{\alpha/(1-\alpha)} \tag{45}$$

$$\left(\frac{\partial P}{\partial\rho}\right)_{T,\mu} = RT_{\mathrm{c}0}\Gamma_0^{-1}\left(\frac{\tau(x)}{X_{\mathrm{A}}}\right)^{\gamma/(1-\alpha)} \tag{46}$$

$$\left(\frac{\partial\mu}{\partial x}\right)_{P,T} \simeq \frac{RT}{xX_\Gamma}\left(\frac{\tau}{X_{\mathrm{A}}}\right)^{\gamma/(1-\alpha)} \simeq \frac{RT}{x^2}\frac{1}{\Gamma_0}\left(\frac{1}{P_{\mathrm{c}}}\frac{dP_{\mathrm{c}}}{dx}\right)^{-2}\left(\frac{\tau(x)}{X_{\mathrm{A}}}\right)^{\gamma/(1-\alpha)} \tag{47}$$

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[2] The second critical condition $(\partial^2\mu/\partial x^2)_{P,T} = 0$ in a dilute limit is provided by vanishing the second derivative $(\partial^2 P/\partial\rho^2)_T \sim x$ [9].

Thus at infinite dilution the range in which $(\partial\mu/\partial x)_{P,T}$ is small shrinks to the critical point of the pure solvent. On the critical line $(\partial\mu/\partial x)_{P,T}=0$ for all x, and the solution cannot be regarded as dilute for any arbitrary low concentration of dissolved substance.

Now we assume the simplest form of a crossover formula for the thermodynamic quantities that incorporates the correct asymptotic behavior expressed by Eqs. (37)–(47):

$$\left(\frac{\partial x}{\partial\mu}\right)_{P,T}=\left\{X_{\Gamma}\left[\frac{\tau(x)}{X_{\mathrm{A}}+\tau^{\alpha}(x)}\right]^{-\gamma/(1-\alpha)}+1\right\}\frac{x}{RT} \tag{48}$$

$$\left(\frac{\partial\rho}{\partial P}\right)_{T,x}=\frac{\Gamma_0}{RT}\left[\frac{X_{\mathrm{A}}}{X_{\Gamma}}\left(\frac{\tau(x)}{X_{\mathrm{A}}+\tau^{\alpha}(x)}\right)^{-\alpha/(1-\alpha)}+\frac{1}{X_{\Gamma}+\tau^{\gamma}(x)}\right] \tag{49}$$

$$C_{P,x}=\Gamma_0\left(\frac{T_{\mathrm{c}}\,dP_{\mathrm{c}}}{P_{\mathrm{c}}\,dT_{\mathrm{c}}}\right)^2\left[\frac{X_{\mathrm{A}}}{X_{\Gamma}}\left(\frac{\tau(x)}{X_{\mathrm{A}}+\tau^{\alpha}(x)}\right)^{-\alpha/(1-\alpha)}+\frac{1}{X_{\Gamma}+\tau^{\gamma}(x)}\right]R \tag{50}$$

$$\left(\frac{\partial x}{\partial\mu}\right)_{\rho,T}=\left[X_{\mathrm{A}}\left(\frac{\tau(x)}{X_{\mathrm{A}}+\tau^{\alpha}(x)}\right)^{-\alpha/(1-\alpha)}+1\right]\frac{x}{RT} \tag{51}$$

The crossover behavior of the critical susceptibility $(\partial x/\partial\mu)_{P,T}$ and isobaric specific heat is shown in Figs. 1 and 2. The values of the system-dependent parameters in Eqs. (48) and (50) here and below were taken for the dilute binary solution metane–ethane (x is the mole fraction of ethane) [10]. As shown in Fig. 1, the smaller x, the narrower the range of strong singularity of the susceptibility $(\partial x/\partial\mu)_{P,T}$. The behavior of the specific heat $C_{P,x}$, as shown in Fig. 2, is characterized by crossover from the strong singularity far away from the critical point to the weak singularity closer to the critical point. The smaller x, the narrower the range of the *weak* singularity of the specific heat $C_{P,x}$.

Finally, we consider the derivative $(\partial\mu/\partial T)_{P,T}$, which plays an important role in the behavior of the transport properties of critical binary mixtures. According to the thermodynamic relation

$$\left(\frac{\partial\mu}{\partial T}\right)_{P,x}=-\left(\frac{\partial\mu}{\partial x}\right)_{P,T}\left[\left(\frac{\partial x}{\partial T}\right)_{\rho,\mu}-\left(\frac{\partial x}{\partial\rho}\right)_{T,\mu}\left(\frac{\partial\rho}{\partial P}\right)_{T,\mu}\left(\frac{\partial P}{\partial T}\right)_{\rho,\mu}\right] \tag{52}$$

where the derivative $(\partial P/\partial T)_{\rho,\mu}=\text{constant}$ at the critical point. For the derivatives $(\partial x/\partial T)_{\rho,\mu}$ and $(\partial x/\partial\rho)_{T,\mu}$, using Eqs. (2), (4), and (31) we obtain

$$\left(\frac{\partial x}{\partial T}\right)_{\rho,\mu}=-\left(\frac{\partial^2 A^*}{\partial T\partial\mu}\right)_{\rho}\simeq-\frac{x\ln x}{T}-X_{\mathrm{A}}\tau(\mu)^{-\alpha}\left(\frac{dT_{\mathrm{c}}}{dx}\right)^{-1} \tag{53}$$

$$\left(\frac{\partial x}{\partial\rho}\right)_{T,\mu}=-\left(\frac{\partial^2 A^*}{\partial T\partial\mu}\right)_{\rho}\simeq-\frac{x}{\rho_{\mathrm{c}}}\left(\frac{1}{P_{\mathrm{c}}}\frac{dP_{\mathrm{c}}}{dx}\right) \tag{54}$$

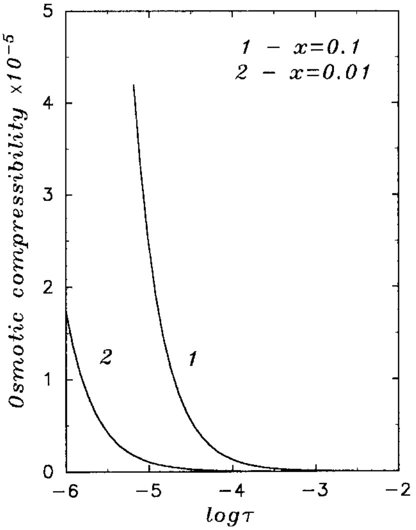

Fig. 1. The critical behavior of the dimensionless "osmotic compressibility" $(1/RT)(\partial x/\partial\mu)_{P,T}$ according to Eq. (48). All the system-dependent parameters herein and hereafter were taken for the mixture methane–ethane (x is the mole fraction of ethane) [10]: $A_0=4.8$, $\Gamma_0=0.2$, $(1/T_c)(dT_c/dx)=0.8$, $(1/P_c)(dP_c/dx)=2$.

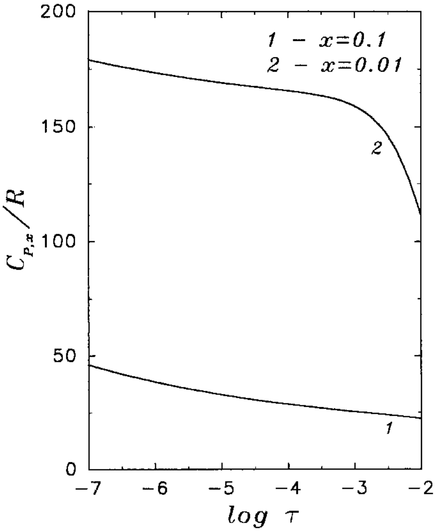

Fig. 2. The critical behavior of the isobaric specific heat $C_{P,x}$ according to Eq. (50).

As can be seen from Eqs. (52)–(54), the behavior of the derivative $(\partial\mu/\partial T)_{P,x}$ is determined by the derivative $(\partial\mu/\partial x)_{P,T}$. At $\tau \ll X_T^{1/\gamma}$ the second term in the brackets on the right-hand side of Eq. (52) dominates, the singularities of $(\partial\mu/\partial x)_{P,T}$ and $(\partial\rho/\partial P)_{T,\mu}$ compensate each other [see Eqs. (6), (12) (16), (43), and (47)], and the value of $(\partial\mu/\partial T)_{P,x}$ remains finite:

$$\left(\frac{\partial\mu}{\partial T}\right)_{P,x} \simeq \frac{R}{x}\frac{T_c}{dT_c/dx} \tag{55}$$

Far away from the critical point [at condition (24)] $(\partial\mu/\partial x)_{P,T} \sim (1/x)$ [see Eq. (39)] and

$$\left(\frac{\partial\mu}{\partial T}\right)_{P,x} \simeq R\ln x \tag{56}$$

i.e., it is also finite. So the derivative $(\partial\mu/\partial T)_{P,x}$ is finite at the critical point of a mixture "in general" and diverges along the critical line as x^{-1} while $x \to 0$.

4. TRANSPORT PROPERTIES

The singularities of transport properties in the critical region are induced by the critical slowing down of the fluctuations in the order parameter. The single temporal scale of this slowing down is the critical relaxation time

$$t_c = \xi^2/\chi \tag{57}$$

where in one-component fluids

$$\chi = \lambda/\rho C_P \tag{58}$$

is the thermal diffusivity, λ is the thermal conductivity, C_P is the isobaric specific heat.

According to the dynamic scaling theory [11]

$$\chi = k_B T/6\pi\tilde{\eta}\xi \tag{59}$$

and

$$\lambda = \frac{k_B T\rho}{6\pi\tilde{\eta}\xi} C_P + \lambda_b \tag{60}$$

where k_B is Boltzmann's constant, $\tilde{\eta}$ is the shear viscosity, and λ_b is the background part of the thermal conductivity, that is, a regular function. The correlation length ξ diverges at the critical point. In the first approximation, one can neglect the possible weak singularity of the shear viscosity and estimate the following behavior of the critical (singular) enhancement of the thermal conductivity [11]

$$\lambda = \lambda_s + \lambda_b \tag{61}$$

$$\lambda_s = \frac{k_B T \rho}{6\pi\tilde{\eta}\xi} C_P \sim \tau^{(-\gamma+\nu)} \tag{62}$$

The simplifications made above allowed Sengers and his co-workers to develop the dynamic scaling theory for description of the thermal conductivity of the various fluids in the wide region around the critical point [12].

In binary mixtures the situation is much more complicated. The Onsager expressions for the diffusion current J_d and heat current J_q in binary mixtures read:

$$J_d = -\tilde{\alpha}\nabla\mu - \tilde{\beta}\nabla T \tag{63}$$

$$J_q = -\tilde{\gamma}\nabla T - T\tilde{\beta}\nabla\mu + J_d\mu \tag{64}$$

where $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ are the Onsager kinetic coefficients. The coefficient $\tilde{\gamma}$ determines the pure heat current at constant chemical potential (when $\nabla\mu = 0$):

$$q = J_q - \mu J_d = -\tilde{\gamma}\nabla T \tag{65}$$

Thus $\tilde{\gamma}$ plays the same role in binary mixtures as λ in one-component fluids. Analogously, the thermal diffusivity of binary mixtures at constant chemical potential can be introduced:

$$\tilde{\chi} = \tilde{\gamma}/\rho C_{P,\mu} \tag{66}$$

where

$$C_{P,\mu} = T\left(\frac{\partial S}{\partial T}\right)_{P,\mu} \tag{67}$$

(S is the molar entropy). The coefficient $\tilde{\alpha}$ is associated with the mutual diffusion in binary mixtures

$$D = (\tilde{\alpha}/\rho)(\partial\mu/\partial x)_{P,T} \tag{68}$$

and can be regarded as a mutual "mobility" of the components.

Generalization of the isomorphism concept to transport phenomena [3, 13] leads to the Einstein–Stokes diffusion expression given by Eq. (59) for both $\tilde{\chi}$ and D asymptotically close to the critical point of a mixture:

$$\tilde{\chi} = D = \frac{k_B T}{6\pi\tilde{\eta}\xi} \tag{69}$$

The Onsager kinetic coefficients $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ diverge at the critical point just as the thermal conductivity at the critical point of a one-component fluid. The mode-coupling calculations performed by Giterman and Gorodetskii [13], and Mistura [14] corroborates this assumption and leads to the following expression for $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$:

$$\tilde{\gamma} = \frac{k_B T^2 \rho}{6\pi\tilde{\eta}\xi}\left(\frac{\partial S}{\partial T}\right)_{P,\mu} + \tilde{\gamma}_b \tag{70}$$

$$\tilde{\beta} = \frac{k_B T \rho}{6\pi\tilde{\eta}\xi}\left(\frac{\partial x}{\partial T}\right)_{P,\mu} + \tilde{\beta}_b \tag{71}$$

$$\tilde{\alpha} = \frac{k_B T \rho}{6\pi\tilde{\eta}\xi}\left(\frac{\partial x}{\partial \mu}\right)_{P,T} + \tilde{\alpha}_b \tag{72}$$

where $\tilde{\gamma}_b$, $\tilde{\beta}_b$, and $\tilde{\alpha}_b$ are background (regular) part of the kinetic coefficients. The thermal conductivity of a mixture is defined by the equations

$$\left.\begin{aligned} q &= -\lambda \nabla T \\ J_d &= 0 \end{aligned}\right\} \tag{73}$$

and related to the kinetic coefficients $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ with the following relation:

$$\lambda = \tilde{\gamma} - (\tilde{\beta}^2/\tilde{\alpha}) \tag{74}$$

Using the thermodynamical relations

$$C_{P,\mu} - C_{P,x} = T\left(\frac{\partial \mu}{\partial T}\right)^2_{P,x}\left(\frac{\partial x}{\partial \mu}\right)_{P,T} \tag{75}$$

$$\left(\frac{\partial x}{\partial T}\right)_{P,\mu} = \left(\frac{\partial \mu}{\partial T}\right)_{P,x}\left(\frac{\partial x}{\partial \mu}\right)_{P,T} \tag{76}$$

we can easily show that the thermal conductivity does not diverge at the critical point of a mixture. Neglecting the background parts of the kinetic coefficients, Mistura [14, 15] obtained the following expression of the asymptotic critical enhancement $\Delta\lambda_c$:

$$\Delta\lambda_c = \frac{k_B T_\rho}{6\pi\eta\xi} C_{P,x} \tag{77}$$

In contrast to one-component fluids, that vanishes at the critical point because $C_{P,x}$ diverges weaker than ξ [see Eqs. (17) and (25)].

Here we show that Mistura's formula for the critical enhancement of the thermal conductivity is not correct. The correct formula can be obtained by including the cross terms between regular and background parts of the kinetic coefficients.[3] Substituting Eqs. (70)–(72) for the kinetic coefficients into Eq. (74), we obtain, by account of Eqs. (75) and (76),

$$\begin{aligned} \lambda = {} & \frac{k_B T\rho}{6\pi\tilde{\eta}\xi} C_{P,x} - (T/\tilde{\alpha}) \left[\tilde{\beta}_b + \left(\frac{\partial\mu}{\partial T} \right)_{P,x} \tilde{\alpha}_b \right]^2 \\ & + T \left(\frac{\partial\mu}{\partial T} \right)_{P,x}^2 \tilde{\alpha}_b + 2T \left(\frac{\partial\mu}{\partial T} \right)_{P,x} \tilde{\beta}_b + \tilde{\gamma}_b \end{aligned} \tag{78}$$

Both the first and the second terms in Eq. (78) vanish at the critical point, however, they provide the divergence of the temperature derivative. The sign of the derivative at the critical point will depend on competition these terms. At the condition given by Eq. (13), in accordance with Eqs. (17) and (25), the first term in Eq. (78) reads

$$\frac{k_B T}{6\pi\tilde{\eta}\xi} C_{P,x} \sim \tau^{(\nu+\phi-\alpha)/(1-\alpha)}(x) \tag{79}$$

where the new exponent ϕ determines the behavior of the shear viscosity of a mixture along the critical isochore:

$$\tilde{\eta} = \tilde{\eta}_b \tau^{-\phi}(\mu) \tag{80}$$

where $\tilde{\eta}_b$ is a viscosity background. For the second term, according to Eqs. (17), (47), and (72), we obtain

$$\frac{T}{\tilde{\alpha}} \left(\tilde{\beta}_b + \left(\frac{\partial\mu}{\partial T} \right)_{P,x} \tilde{\alpha}_b \right)^2 \sim \tau^{(\gamma-\nu-\phi)/(1-\alpha)}(x) \tag{81}$$

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[3] This is also shown by Mostert and Sengers [16].

Since $\gamma = (2-\eta)\,\nu$, the difference of the exponents in Eqs. (79) and (81) is

$$\Delta = \frac{\gamma-\nu-\phi}{1-\alpha} - \frac{\nu+\phi-\alpha}{1-\alpha} = \frac{\alpha-\eta\nu-2\phi}{1-\alpha} \tag{82}$$

Using the theoretical values of the critical exponents α, γ, and ν, we conclude that $\Delta \simeq 0.1$ if the viscosity $\tilde{\eta}$ in Eqs. (70)–(72) remains constant in the critical point or $\Delta \simeq 0$ (within the accuracy of the critical-exponent values), where $\tilde{\eta}$ is the usual low-frequency shear viscosity ($\phi = 0.042$ [17]). In both cases asymptotically close to the critical point the corresponding critical exponents characterizing the two singular terms are practically equal and their competition will strongly depend on the values of amplitudes. It is important to note that exactly at the critical point the value of the thermal conductivity λ_{cb} (we call it the "critical background") is determined by the regular part of the kinetic coefficients as well as by the thermodynamic derivative $(\partial\mu/\partial T)_{P,T}$:

$$\lambda_{\mathrm{cb}} = T\left(\frac{\partial\mu}{\partial T}\right)^2_{P,x} \tilde{\alpha}_{\mathrm{b}} + 2T\left(\frac{\partial\mu}{\partial T}\right)_{P,x} \tilde{\beta}_{\mathrm{b}} + \tilde{\gamma}_{\mathrm{b}} \tag{83}$$

To calculate the thermo- and barodiffusivity we represent the diffusion current in the following form:

$$J_{\mathrm{d}} = D\nabla x - k_{\mathrm{T}} D\nabla T - k_{\mathrm{P}} D\nabla P \tag{84}$$

where

$$k_{\mathrm{T}} D = (\tilde{\alpha}T/\rho)\left(\frac{\partial\mu}{\partial T}\right)_{P,T} + \tilde{\beta}T/\rho \tag{85}$$

$$k_P D = (\tilde{\alpha}/\rho P)\left(\frac{\partial\mu}{\partial P}\right)_{x,T} \tag{86}$$

Taking into account the connection between the singular part of $\tilde{\alpha}$ and $\tilde{\beta}$ [see Eqs. (71) and (72)], we obtain asymptotically close to the critical point that the thermal diffusivity

$$D_T = k_T D = \frac{T}{\rho}\,[\tilde{\beta}_{\mathrm{b}} + \tilde{\alpha}_{\mathrm{b}}(\partial\mu/\partial T)_{x,P}] = \text{constant} \tag{87}$$

and the barodiffusivity

$$D_P = k_P D \sim \tilde{\alpha} \to \infty \tag{88}$$

5. TRANSPORT PROPERTIES OF DILUTE SOLUTIONS

In dilute solutions ($x \ll 1$), the explicit concentration dependence for regular and singular parts of the kinetic coefficients and thermodynamic derivatives are known. Far away from the critical point $\tilde{\alpha} \simeq \tilde{\alpha}_{\mathrm{b}}$, $(\partial \mu / \partial x)_{P,T} \sim x^{-1}$ [Eq. (39)] and the diffusion coefficient, according to its definition, Eq. (68),

$$D = \frac{\tilde{\alpha}_{\mathrm{b}} RT}{\rho x} = \frac{\tilde{\alpha}_0 RT}{\rho} \tag{89}$$

where

$$\tilde{\alpha}_{\mathrm{b}} = \tilde{\alpha}_0 x \qquad \text{and} \qquad \tilde{\alpha}_0 \simeq \frac{1}{6\pi \tilde{\eta}_{\mathrm{b}} \xi_0 N_{\mathrm{A}}}$$

(N_{A} is Avogadro's number). Equation (89) corresponds to the well-known dilute-solution limit for the diffusion coefficient

$$D = D_0 = bRT \tag{90}$$

where $b = \tilde{\alpha}_0 / \rho$ is the molecular mobility. The regular part of $\tilde{\beta}$ manifests the concentration dependence similar to $\tilde{\alpha}_{\mathrm{b}}$:

$$\tilde{\beta}_{\mathrm{b}} = \tilde{\beta}_0 x \tag{91}$$

As for the regular part of $\tilde{\gamma}$, it is, within the accuracy of correction of order of x, equal to the regular part of the thermal conductivity:

$$\tilde{\gamma}_{\mathrm{b}} = \lambda_{\mathrm{b}} + T \left(\frac{\tilde{\beta}_0^2}{\tilde{\alpha}_0} \right) x \tag{92}$$

In this region the singular parts of $\tilde{\alpha}$ and $\tilde{\beta}$ are much less then the regular ones and the thermal conductivity of a mixture behaves as that of a one-component fluid. The opposite case is the immediate vicinity of critical point. In the region ($\tau \ll X_{\mathrm{A}}^{1/\alpha}$), according to Eqs. (72), (47), and (17),

$$\begin{aligned} \tilde{\alpha} &= \tilde{\alpha}_0 x^2 \Gamma_0 \left(\frac{1}{P_{\mathrm{c}}} \frac{dP_{\mathrm{c}}}{dx} \right)^2 \left(\frac{\tau}{X_{\mathrm{A}}} \right)^{-(\gamma - \nu - \phi)/(1-\alpha)} + \tilde{\alpha}_0 x \\ &= \tilde{\alpha}_{\mathrm{b}} X_{\Gamma} \left(\frac{\tau}{X_{\mathrm{A}}} \right)^{-(\gamma - \nu - \phi)/(1-\alpha)} + \tilde{\alpha}_0 x \end{aligned} \tag{93}$$

and the critical background of the thermal conductivity is

$$\lambda_{\mathrm{cb}} = \lambda_{\mathrm{b}} + T(\tilde{\beta}_0^2 / \tilde{\alpha}_0)\, x + 2RT_{\mathrm{c}}^2 \tilde{\beta}_0 (dT_{\mathrm{c}}/dx)^{-1} + \tilde{\alpha}_0 A_0 T_{\mathrm{c}} R^2 X_{\mathrm{A}}^{-1} \tag{94}$$

Since the first three terms in Eq. (94) become constant upon approaching the critical point of the solvent and $X_{\mathrm{A}} \sim X_{\Gamma}$, the critical background of the thermal conductivity diverges along the critical line as x^{-1}. Asymptotically close to the critical point

$$\lambda = \lambda_{\mathrm{cb}} - \frac{T_{\mathrm{c}} R^2 \tilde{\alpha}_0}{X_{\mathrm{A}} X_{\Gamma}} \left(\frac{\tau}{X_{\mathrm{A}}} \right)^{(\gamma - \nu - \phi)/(1-\alpha)} + T_{\mathrm{c}} R^2 \tilde{\alpha}_0 \left(\frac{\tau}{X_{\mathrm{A}}} \right)^{(\nu - \alpha + \phi)/(1-\alpha)} \tag{95}$$

In the case of divergent $\tilde{\eta}$, as shown above [Eq. (82)], the exponents of the two singular terms in Eq. (95) are practically equal and in dilute solutions the negative term is dominant. Since $X_{\mathrm{A}} \sim X_{\Gamma} \sim x$, the thermal conductivity has a cusp diverging as x^{-1} approaching the critical point of a solvent with the infinite temperature derivative, whose amplitude diverges as x^{-2}. In the case of a nondivergent $\tilde{\eta}$ the situation is determined by the competition of these terms. Experimentally the first term will dominate anyway at sufficiently small concentrations. So very close to the critical point of a solvent (see Fig. 3),

$$\lambda_{\mathrm{cb}} \simeq \tilde{\alpha}_0 A_0 T_{\mathrm{c}} R^2 X_{\mathrm{A}}^{-1} \tag{96}$$

and

$$\lambda \simeq T_{\mathrm{c}} R^2 \tilde{\alpha}_0 A_0 X_{\mathrm{A}}^{-1} \left[1 - X_{\Gamma}^{-1} \left(\frac{\tau}{X_{\mathrm{A}}} \right)^{(\gamma - \nu - \phi)/(1-\alpha)} \right] \tag{97}$$

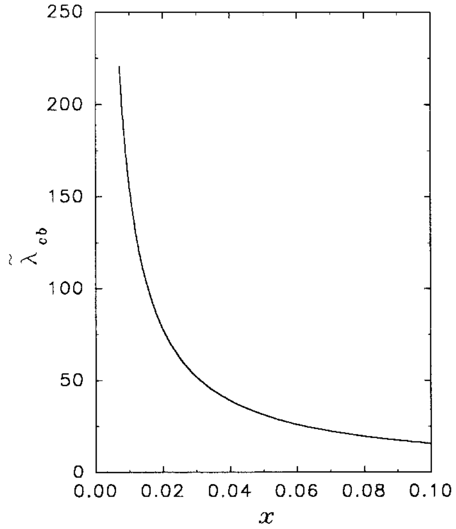

Fig. 3. The dimensionless critical background $\tilde{\lambda}_{\mathrm{cb}} = \lambda_{\mathrm{cb}} / \tilde{\alpha}_0 R^2 T_{\mathrm{c}}$ of the thermal conductivity of a mixture according to Eq. (96).

which may be compared with the corresponding expression for the renormalized isochoric specific heat [see Eq. (18)]. The diffusion coefficient

$$D=\frac{k_B T}{6\pi\tilde{\eta}\xi}=\frac{\tilde{\alpha}_0 RT}{\rho}\left(\frac{\tau}{X_A}\right)^{(\nu+\phi)/(1-\alpha)} \tag{98}$$

The thermo- and barodiffusivity

$$D_T \simeq \frac{\tilde{\alpha}_0 RT}{\rho}+\frac{T\tilde{\beta}_0 x}{\rho} \to D_0=\text{constant} \tag{99}$$

$$D_P \simeq \frac{\Gamma_0 RT\tilde{\alpha}_0 x}{\rho}\left(\frac{dP_c}{P_c\,dx}\right)\left(\frac{\tau}{X_A}\right)^{-(\gamma-\nu-\phi)/(1-\alpha)} \tag{100}$$

The crossover from one-component-like behavior to mixture-like behavior takes place in the range $X_A^{1/\alpha} \leqslant \tau \leqslant X_\Gamma^{1/\gamma}$. In this region the situation depends on the competition between the singular and the regular parts of the transport properties (see also Ref. 18). The explicit form of the crossover for the thermal conductivity from one-component-like behavior to mixture-like behavior can be obtained using the dilute-limit expressions for all terms entering Eq. (78) and the approximate solution of Eq. (9) $(\tau^{1-\alpha}(\mu)=\tau(x)[X_A+\tau^\alpha(x)]^{-1})$:

$$\Delta\tilde{\lambda}=\frac{\lambda-\lambda_b}{\tilde{\alpha}_0 R^2 T_c}=\Gamma_0\left(\frac{T_c}{P_c}\frac{dP_c}{dT_c}\right)^2\left[\frac{X_A}{X_\Gamma}\left(\frac{\tau}{X_A+\tau^\alpha}\right)^{-\alpha/(1-\alpha)}+\frac{1}{X_\Gamma+\tau^\gamma}\right]$$
$$\times\left(\frac{\tau}{X_A+\tau^\alpha}\right)^{(\nu+\phi)/(1-\alpha)}+x\left[1+\frac{(\partial\mu/\partial T)_{P,x}}{R}\right]^2 Y(\tau)$$

where

$$Y(\tau)=1-\left\{1+\left(\frac{\tau}{X_A+\tau^\alpha}\right)^{(\nu+\phi)/(1-\alpha)}\left[1+X_\Gamma\left(\frac{\tau}{X_A+\tau^\alpha}\right)^{-\gamma/(1-\alpha)}\right]\right\}^{-1} \tag{101}$$

Within the "cone" $\tau < X_\Gamma^{1/\gamma}$, using the expression for $(\partial\mu/\partial T)_{P,x}$ given by Eq. (55), we have

$$\Delta\tilde{\lambda}=\frac{A_0}{X_A}\left(\frac{\tau}{X_A+\tau^\alpha}\right)^{(\nu+\phi)/(1-\alpha)}\left[X_A\left(\frac{\tau}{X_A+\tau^\alpha}\right)^{-\alpha/(1-\alpha)}+\frac{X_\Gamma}{X_\Gamma+\tau^\gamma}\right]$$
$$+\frac{A_0}{X_A}\left(1+\frac{x}{T_c}\frac{dT_c}{dx}\right)^2 Y(\tau) \tag{102}$$

The crossover behavior of the thermal conductivity in critical dilute mixtures is shown in Fig. 4. One can see that the higher the solute concen-

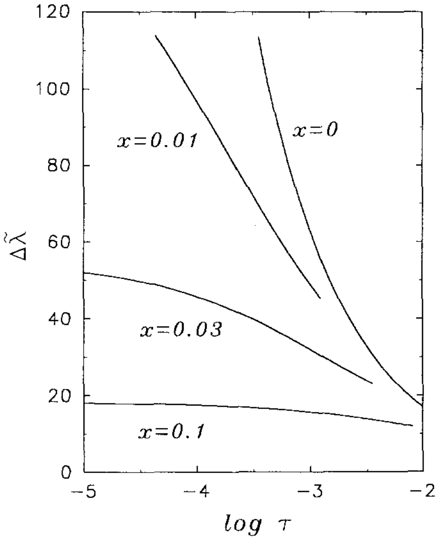

Fig. 4. The critical enhancement of the thermal conductivity $\Delta\tilde{\lambda}=(\lambda-\lambda_b)/\tilde{\alpha}_0 R^2 T_c$ in critical mixtures according to Eq. (101).

tration, the smaller the thermal-conductivity enhancement. However, even for $x=0.1$ the pronounced critical enhancement still exists. When $\tau \gg X_\Gamma^{1/\gamma}$, Eq. (101) with account of Eq. (56) reads

$$\Delta\tilde{\lambda}=\Gamma_0\left(\frac{T_c}{P_c}\frac{dP_c}{dT_c}\right)^2 \tau^{-\gamma+\nu+\phi}(x) \tag{103}$$

and the thermal conductivity of a mixture behaves as that of a one-component fluid.

6. CONCLUSION

All thermophysical properties in binary mixture can be divided into three groups.

Isomorphic: $C_{P,\mu}, C_{V,\mu}, \left(\frac{\partial P}{\partial\rho}\right)_{T,\mu}, \xi, \tilde{\gamma}, \tilde{\eta}, \tilde{\chi}$

Nonisomorphic: $C_{V,x}, C_{P,x}, \left(\frac{\partial P}{\partial\rho}\right)_{T,x}, \lambda, \chi$

Special: $\left(\frac{\partial\mu}{\partial x}\right)_{P,T}, \left(\frac{\partial\rho}{\partial x}\right)_{P,T}, \left(\frac{\partial\mu}{\partial T}\right)_{P,x}, \tilde{\alpha}, \tilde{\beta}, D$

The isomorphic values behave as the corresponding values behave in one-component fluids. The only difference is the renormalization of the thermodynamic path at constant concentration ($\tau \rightarrow \tau^{1/(1-\alpha)}$). The non-isomorphic values behave differently from those in one-component fluids: e.g., $C_{V,x}$ and λ remain finite, and $C_{P,x}$ and $(\partial\rho/\partial P)_{T,x})$ diverge weakly. The special values exist only in mixtures and manifest the critical behavior only in the narrow interval of τ dependent on x (concentration of a mixture). The lower the concentration, the narrower the interval of their critical behavior. The dilute-solution limit provides an opportunity to write in the explicit concentration-dependent form the crossover functions from one-component-like behavior to mixture-like behavior. However, it should be emphasized that all formulae presented above have been obtained at the limit $\tau \ll 1$. It means that even "far away from the critical point" in accordance with $\tau \gg X_T^{1/\gamma}$, we should keep in mind that the limit $\tau \ll 1$ is assumed throughout anyway. For the description of the entirely wide region around the critical line, one needs the other crossover problem to be solved: the crossover from analytical regular behavior far away from the critical point to the nonanalytical (critical) behavior. This problem can be regarded as solved "in principle" for thermodynamic as well as for transport properties of one-component fluids [2, 19, 20] but it is still being formulated for binary mixtures [21]. Although the existing experimental rsults on the thermal conductivity of mixtures [22–24] are in qualitative agreement with the theory developed in this paper, more experimental studies in the entire neighborhood of the vapor–liquid critical line are needed for the quantitative description of transport coefficients of near-critical mixtures.

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