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Crossover Behavior of the Transport Coefficients of Critical Binary Mixtures

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The behavior of the transport coefficients related to diffusion, heat conduction, and their cross-processes in fluid mixtures near the consolute point and the liquid–vapor critical line is investigated. Simple crossover equations for the critical enhancement of those coefficients are developed by incorporating a finite cutoff and time-dependent correlation functions of the order parameter and of the entropy into decoupled-mode theory integrals. It is shown that the thermal conductivity of a binary mixture is nondivergent and the crossover from the critical background in the critical point to the regular background far from the critical point is elucidated. The crossover to the behavior of the thermal conductivity in the one-component limit is also discussed.

KEY WORDS: binary mixtures; critical phenomena; ethane; methane; thermal conductivity; transport coefficients.

1. INTRODUCTION

It is well-known that the state of a fluid near a critical point is characterized by anomalous large fluctuations of the order parameter. In accordance with the main concept of scaling theory [1, 2], the only size characterizing the fluctuations is the equilibrium correlation length ξ, which diverges at a critical isochore of a one-component fluid as

$$\xi = \xi_0 \tau^{-\nu} \tag{1}$$

where $\tau = T/T_c - 1$ is the dimensionless deviation of the temperature T from the critical value T_c, ξ_0 is a system-dependent parameter, and $\nu \simeq 0.63$

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is a universal critical exponent. As a consequence both thermodynamic and transport properties of a fluid in the vicinity of the critical point exhibit singular power-law behavior [3–6]. The mode-coupling theory of critical dynamics yields the following integral for the singular contribution to the thermal diffusivity $D_T = \lambda/\rho C_P$ [7–9]:

$$\Delta D_T(q) = \frac{\Delta\lambda(q)}{\rho C_P(q)} = \frac{k_B T}{(2\pi)^3 \rho} \int_0^{q_D} d\vec{k} \left[\frac{C_P(|\vec{q}-\vec{k}|)}{C_P(q)}\right] \times \frac{\sin^2\Theta}{k^2\eta(k)/\rho + |\vec{q}-\vec{k}|^2 D_T(|\vec{q}-\vec{k}|)} \tag{2}$$

where $\Delta\lambda = \lambda - \lambda_b$ is the singular part of the thermal conductivity λ, λ_b the regular or background part, η the shear viscosity, ρ the density, C_P the isobaric specific heat, k_B Boltzmann's constant, and $\vec{q}$ the wave vector of the fluctuations, while Θ is the polar angle of $\vec{k}$ with respect to $\vec{q}$. The integral is to be evaluated over all k up to maximum cutoff wave number $q_D = |\vec{q}_D|$ first introduced by Perl and Ferrell [10]. With an infinite cutoff a calculation of the integral in Eq. (2) yields

$$\Delta D_T(q) = \frac{\Delta\lambda(q)}{\rho C_P(q)} = \frac{k_B T}{6\pi\eta\xi} \Omega_K(q\xi) \tag{3}$$

where $\Omega_K(z) = (3/4z^2)[1 + z^2 + (z^3 - z^{-1})\arctan(z)]$ is the so-called Kawasaki function [7, 9]. In the hydrodynamic limit $q \to 0$ Eq. (3) takes the form of the well-known Stokes–Einstein relation [9, 11]

$$\Delta D_T = \frac{\Delta\lambda}{\rho C_P} = \frac{k_B T}{6\pi\eta\xi} \tag{4}$$

The validity of this equation is restricted to a very small range of temperatures and densities near the critical point. To present the actual behavior of the thermal conductivity of one-component fluids in a wide region of temperatures and densities, one should provide the integration with a finite cutoff. In this case Eq. (2) reads

$$\frac{\Delta\lambda}{\rho C_P} = \frac{k_B T}{6\pi\eta\xi} \Omega(q_D\xi) \tag{5}$$

where the dynamic crossover function $\Omega(q_D\xi)$ arises from the integration of Eq. (2) over $\vec{k}$ with a finite cutoff q_D in the limit $q \to 0$. However, the integral in Eq. (2) cannot be evaluated rigorously without any additional assumptions [12–14]. A simplified approximation of this integral has been obtained by Olchowy and Sengers [13]:

$$\Omega_{\mathrm{OS}}(q_D\xi)=\frac{2}{\pi}\left\{\left(\frac{C_{\mathrm{P}}-C_{\mathrm{v}}}{C_{\mathrm{P}}}\right)\arctan(q_D\xi)+\frac{C_{\mathrm{v}}}{C_{\mathrm{P}}}q_D\xi-1\right.$$
$$\left.+\exp\left[-\frac{1}{(q_D\xi)^{-1}+((\rho_{\mathrm{c}}/\rho)\,q_D\xi)^2/3}\right]\right\} \tag{6}$$

where C_{v} is the isochoric specific heat and ρ_{c} is the critical density. A similar result has been obtained for the shear viscosity [15]. A more general solution for the shear viscosity has been obtained by Olchowy and Sengers [12].

The situation in binary mixtures is more complicated. The Onsager expressions for the diffusion current $\vec{J}_{\mathrm{d}}$ and heat current $\vec{J}_{\mathrm{q}}$ in binary mixtures read [16]

$$\vec{J}_{\mathrm{d}}=-\tilde{\alpha}\,\nabla\mu-\tilde{\beta}\,\nabla T \tag{7}$$

$$\vec{J}_{\mathrm{q}}=-\tilde{\beta}T\,\nabla\mu-\tilde{\gamma}\,\nabla T+\mu\vec{J}_{\mathrm{d}} \tag{8}$$

where $\mu=\mu_2-\mu_1$ is the chemical potential of the mixture and where $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ are Onsager kinetic coefficients. Mode-coupling calculations performed by Gorodetskii and Giterman [17] and Mistura [18, 19] show that asymptotically close to the critical point, the Onsager kinetic coefficients diverge as the thermal conductivity of a one-component fluid,

$$\Delta\tilde{\alpha}=\tilde{\alpha}-\tilde{\alpha}_{\mathrm{b}}=\frac{k_{\mathrm{B}}T\rho}{6\pi\eta\xi}\left(\frac{\partial x}{\partial\mu}\right)_{P,T} \tag{9}$$

$$\Delta\tilde{\beta}=\tilde{\beta}-\tilde{\beta}_{\mathrm{b}}=\frac{k_{\mathrm{B}}T\rho}{6\pi\eta\xi}\left(\frac{\partial x}{\partial T}\right)_{P,\mu} \tag{10}$$

$$\Delta\tilde{\gamma}=\tilde{\gamma}-\tilde{\gamma}_{\mathrm{b}}=\frac{k_{\mathrm{B}}T\rho}{6\pi\eta\xi}\left(\frac{\partial S}{\partial T}\right)_{P,\mu} \tag{11}$$

where $x=N_2/(N_1+N_2)$ is the mole fraction of the second component, S is the molar entropy of the mixture, and the subscript "b" denotes the background part of the transport coefficient, which is not influenced by critical fluctuations. However, the crossover expressions for the transport coefficients of a binary mixture analogous to Eq. (5) for the thermal conductivity of a one-component fluid have not yet been obtained [17–19]. It is the purpose of this paper to present the crossover functions for the transport coefficients $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ in critical binary mixtures. In evaluating these crossover functions we use the method of the dynamical scaling theory originally introduced by Ferrell [11].

In Section 2 within the Gaussion approximation we obtain the time-dependent correlation functions for the velocity and for the order parameter. Using approximate solutions for the correlation functions we derive in Sections 3 and 4 simple expressions for the crossover functions of the transport coefficients in a binary mixture. The obtained relations have the same form as the crossover function for the thermal-conductivity enhancement for a one-component fluid. In Section 5 we analyze the crossover behavior of the thermal conductivity near the liquid–vapor critical point of binary mixtures on the basis of the isomorphism hypothesis [20]. A comparison with experimental thermal-conductivity data for pure ethane is given in Section 6.

2. EQUATIONS FOR THE TRANSPORT COEFFICIENTS

To obtain the crossover expressions for the transport coefficient in binary mixtures, it is convenient to start from the correlation-function expressions of the fluctuation-dissipation theorem (also-called "Kubo formulas"). Using the notation of Refs. 18 and 19 we have

$$\tilde{\alpha} = \frac{1}{6k_B T} \int d\vec{r} \int dt \langle \vec{J}_d(0, 0)\, \vec{J}_d(\vec{r}, t) \rangle \tag{12}$$

$$\tilde{\beta} = \frac{1}{6k_B T^2} \int d\vec{r} \int dt \langle \vec{J}_d(0, 0)\, \vec{J}_S(\vec{r}, t) \rangle \tag{13}$$

$$\tilde{\gamma} = \frac{1}{6k_B T^2} \int d\vec{r} \int dt \langle \vec{J}_S(0, 0)\, \vec{J}_S(\vec{r}, t) \rangle \tag{14}$$

where $\vec{J}_d$ and $\vec{J}_S$ are the microscopic diffusion and heat currents. The next step is connected with a "decoupled-mode" approximation in the spirit of Ferrell's work [11]. Since the concentration and entropy density are slow variables near a critical point, we may treat them as independent from the velocity fluctuations in the current–current correlation functions. This approach takes into account only singular behavior of the transport properties. If $\vec{J}_d = \rho\, \delta x \vec{v}$ and $\vec{J}_S = T\rho\, \delta S \vec{v}$ (where δx and δS denote the deviations of concentration and local entropy from the equilibrium values), Eqs. (12)–(14) transform to

$$\Delta\tilde{\alpha} = \frac{\rho^2}{6k_B T} \int d\vec{r} \int dt \langle \delta x(0, 0)\, \delta x(\vec{r}, t) \rangle \langle \vec{v}(0, 0)\, \vec{v}(\vec{r}, t) \rangle \tag{15}$$

$$\Delta\tilde{\beta}=\frac{\rho^2}{6k_{\mathrm{B}}T}\int d\vec{r}\int dt\langle\delta x(0,0)\,\delta S(\vec{r},t)\rangle\langle\vec{v}(0,0)\,\vec{v}(\vec{r},t)\rangle \tag{16}$$

$$\Delta\tilde{\gamma}=\frac{\rho^2}{6k_{\mathrm{B}}}\int d\vec{r}\int dt\langle\delta S(0,0)\,\delta S(\vec{r},t)\rangle\langle\vec{v}(0,0)\,\vec{v}(\vec{r},t)\rangle \tag{17}$$

The current–current correlation functions in Eqs. (12)–(14) are simplified by the splitting (or in other words, by the factoring) of each current–current correlator into two parts (see Eqs. (15)–(17)).

At the consolute point of a binary mixture we may neglect the density fluctuations that correspond to the condition $(\nabla\cdot\vec{v})=0$. This condition means that only the transverse motion of fluid will be examined. To establish the behavior of the velocity correlations, we may restrict ourselves to the linearized hydrodynamics equation

$$\frac{\partial\vec{v}(\vec{r},t)}{\partial t}=\frac{\eta}{\rho}\nabla^2\vec{v}(\vec{r},t) \tag{18}$$

where η is a high-frequency shear viscosity which is finite at the critical point [11]. This equation looks like the diffusion equation [1] and, hence, in the hydrodynamic limit $k\rightarrow 0$, we have

$$\langle\vec{v}(0,0)\,\vec{v}(\vec{r},t)\rangle=\frac{k_{\mathrm{B}}T}{4\rho}\frac{1}{\sqrt{(\pi\nu t)^3}}\exp\left(-\frac{r^2}{4\nu t}\right) \tag{19}$$

with $\nu=\eta/\rho$. Very close to the critical point the relaxation time of the fluctuations is extremely large, and in a zero approximation we may replace the time-dependent correlations of the concentration and entropy on the right-hand side of Eqs. (15)–(17) with the corresponding static correlation functions. In this case we simply reproduce Mistura's results in the form (9)–(11). As far as we are interested in the crossover behavior of the kinetic coefficients, the time-dependent correlators for the concentration and entropy in Eqs. (15)–(17) should be considered. Since at the critical point the most slowly relaxing variable is the order parameter, first we should obtain the equation of motion for the order parameter. The simplest nonlinear model consistent with the conservation laws of a binary fluid model, denoted model H in Refs. 5 and 21, is defined by the following equations:

$$H=\int d\vec{r}\left[a\tau\frac{\varphi^2}{2}+\frac{c}{2}(\nabla\varphi)^2+\frac{u}{4}\varphi^4+\frac{1}{2}\vec{j}^2\right] \tag{20}$$

$$\frac{\partial\varphi(\vec{r},t)}{\partial t}=\frac{\tilde{\alpha}_0}{\rho^2}\nabla^2\left(\frac{\delta H}{\delta\varphi}\right)-g_0\vec{\nabla}\varphi\frac{\delta H}{\delta\vec{j}}+\zeta(\vec{r},t)\tag{21}$$

$$\frac{\partial\vec{j}(\vec{r},t)}{\partial t}=\mathrm{T}\left(\eta_0\nabla^2\left(\frac{\delta H}{\delta\vec{j}}\right)+g_0\vec{\nabla}\varphi\frac{\delta H}{\delta\varphi}+\vec{\zeta}_1(\vec{r},t)\right)\tag{22}$$

The scalar field $\varphi(\vec{r},t)=x(\vec{r},t)-x_c(P)$ [here $x_c(P)$ is the critical concentration as a function of pressure P] is the order parameter, the transverse vector field $\vec{j}$ corresponds to the momentum density or velocity in an incompressible fluid, and g_0 is a coupling constant. The matrix T is a projection operator which selects the transverse part of the vector in brackets, and $\zeta(\vec{r},t)$ and $\vec{\zeta}_1(\vec{r},t)$ are Gaussian noise sources. The background or bare viscosity and the bare order-parameter transport coefficient are given by η_0 and $\tilde{\alpha}_0$, respectively. This model is very close to the one introduced in the mode-coupling theory [7–9]. As has been shown by Ferrell [11, 22], the "decoupled-mode" approximation (15) is mathematically equivalent to the mode-coupling calculations. The main difference is that the coupling ensured in the mode-coupling theory from the equation of continuity, which connects the current with changes in the density variable, in the "decoupled-mode" theory is automatically taken into account by the Kubo formulas (12)–(14). Therefore, to obtain the time dependence of the order parameter correlation function, one can neglect the coupling in the dynamical equations, which corresponds to the zero value of the coupling constant g_0 in Eqs. (20–22), and consider the effective Hamiltonian of the system in the Landau–Ginzburg form [1];

$$H=\int d\vec{r}\left[a\tau\frac{\varphi^2}{2}+\frac{c}{2}(\nabla\varphi)^2+\frac{u}{4}\varphi^4-h\varphi\right]\tag{23}$$

where the ordering field $h=\mu-\mu_c$ and where μ_c is the value of the chemical potential of a mixture μ in the critical point. The equation of motion for the conserved order parameter has the form of a linear Langevin equation [2],

$$\frac{\partial\varphi(\vec{r},t)}{\partial t}=\frac{\tilde{\alpha}}{\rho^2}\nabla^2\left(\frac{\delta H}{\delta\varphi}\right)+\zeta(\vec{r},t)\tag{24}$$

and Eq. (22) transforms to the linearized hydrodynamic Eq. (18) introduced above. Since the correlation functions will be evaluated in the Gaussian approximation ($u=0$), we may omit the term $\sim\varphi^4$ in Eq. (23). Then Eq. (24) in terms of Fourier components becomes

$$\frac{\partial\delta\varphi_{\vec{k}}(t)}{\partial t}=-\tilde{\alpha}_{\vec{k}}\rho\;{}^2k^2(a\tau+ck^2)\,\delta\varphi_{\vec{k}}(t)+\zeta_{\vec{k}}(t)\tag{25}$$

The solution of Eq. (25),

$$\delta\varphi_{\vec{k}} = \int_{-\infty}^{t} e^{-\tilde{\alpha}_{\vec{k}}\rho^{-2}k^{2}(a\tau + ck^{2})(t-t')}\zeta_{\vec{k}}(t')\,dt' \tag{26}$$

together with the normalization,

$$\langle \zeta_{\vec{k}}(t)\,\zeta_{\vec{k}'}(t')\rangle = 2k_{\mathrm{B}}T\tilde{\alpha}_{\vec{k}}k^{2}\delta_{\vec{k},-\vec{k}'}\delta(t-t') \tag{27}$$

yields

$$\langle \delta\varphi_{\vec{k}'}(0)\,\delta\varphi_{\vec{k}}(t)\rangle = G(k)\exp\left(-\frac{k_{\mathrm{B}}T\tilde{\alpha}_{\vec{k}}k^{2}t}{\rho^{2}G(k)}\right)\delta_{\vec{k},-\vec{k}'} \tag{28}$$

where

$$G(k) = \frac{k_{\mathrm{B}}T}{a\tau + ck^{2}} = \frac{k_{\mathrm{B}}T}{[1+(k\xi)^{2}]\rho}\left(\frac{\partial x}{\partial\mu}\right)_{P,T} \tag{29}$$

is a static correlation function of the order parameter $G(k) = \langle|\delta\varphi_{\vec{k}}|^{2}\rangle$ (so-called Ornstein–Zernike function), and $\xi = \sqrt{c\rho^{-1}(\partial x/\partial\mu)_{P,T}}$ is a correlation length in this approximation.

3. THE CROSSOVER FUNCTION FOR THE TRANSPORT COEFFICIENT $\tilde{\alpha}$

Equation (15) together with Eqs. (19) and (28) for the time-dependent correlation functions $\langle\vec{v}(0,0)\,\vec{v}(\vec{r},t)\rangle$ and $\langle\delta\varphi_{\vec{k}'}(0)\,\delta\varphi_{\vec{k}}(t)\rangle$ completely determines the crossover behavior of the transport coefficient $\tilde{\alpha}$. Substitution of Eqs. (28) and (19) into Eq. (15) and integration over the variables $\vec{r}$ and t yields

$$\Delta\tilde{\alpha} = \frac{\rho}{12\pi^{3}}\int_{0}^{q_D} d\vec{k}\,\frac{G(k)}{k^{2}[\nu + k_{\mathrm{B}}T\tilde{\alpha}_{\vec{k}}\rho^{-2}G^{-1}(k)]} \tag{30}$$

For the mutual diffusion coefficient $D = \tilde{\alpha}\rho^{-1}(\partial x/\partial\mu)_{P,T}$, Eq. (30) reads

$$\Delta D = \frac{\Delta\tilde{\alpha}}{\rho}\left(\frac{\partial\mu}{\partial x}\right)_{P,T} = \frac{k_{\mathrm{B}}T}{12\pi^{3}\rho}\int_{0}^{q_D} d\vec{k}\left[\frac{\chi(k)}{\chi(0)}\right]\frac{1}{k^{2}\eta/\rho + k^{2}D(k)} \tag{31}$$

where we have introduced the notations $\chi(0) = (\partial x/\partial\mu)_{P,T}$, $\chi(k) = \chi(0)/(1+k^{2}\xi^{2})$, and $D(k) = \tilde{\alpha}_{\vec{k}}/\rho\chi(k)$. We note that Eq. (31) with account of the replacement $\chi(k)$ on $C_P(k)$, $\chi(0)$ on $C_P(0)$, and $\Delta\tilde{\alpha}$ on $\Delta\lambda$ is identical to the mode-coupling integral (2) after integration over the angle variable

Θ in the limit $q = 0$. The k-dependent diffusion coefficient $\Delta D(k)$, similar to the thermal diffusivity $\Delta D_T(k)$ of the one-component fluids, satisfies an equation of the form [11, 12]

$$\Delta D(k) = \frac{k_B T}{6\pi\eta\xi} \Omega_K(z) \tag{32}$$

with $z = k\xi$. For the transport coefficient $\Delta\tilde{\alpha}(k)$, Eq. (32) reads

$$\Delta\tilde{\alpha}(k) = \Delta D(k)\, \rho\chi(k) = \frac{k_B T \rho}{6\pi\eta\xi} \left(\frac{\partial x}{\partial \mu}\right)_{P,T} \sigma(z) \tag{33}$$

with the dynamical scaling function

$$\sigma(z) = \Omega_K(z)/(1 + z^2) \tag{34}$$

In the hydrodynamic regime ($z \ll 1$) the function $\sigma(z) \cong \sigma(0) = 1$, and in the "critical regime" ($z \to \infty$) the scaling function $\sigma(\infty) = 0$. The variation of $\sigma(z)$ between these two limits at intermediate values of z is shown in Fig. 1. Over the whole range of the scaling variable $\infty > z > 0$, the dynamical scaling function $\sigma(z)$ is changed smoothly from unity to zero, and it differs significantly from unity only in the asymptotical critical region at $z \gg 1$.

The nontrivial dependence of the transport coefficient $\alpha_{\vec{k}}$ on $\vec{k}$ makes the integral in Eq. (30) just too complicated for further analytical calcula-

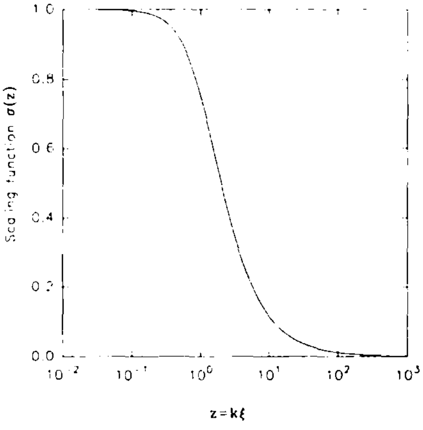

Fig. 1. Dynamical scaling function $\sigma(z)$ for the transport coefficient $\Delta\tilde{\alpha}(k)$ as defined by Eq. (34).

tions. The k-dependent transport coefficient $\tilde{\alpha}_{k}$, similar to the transport coefficient $\tilde{\alpha}$ [see Eq. (9)], can be represented in the form

$$\tilde{\alpha}_{k} = \Delta\tilde{\alpha}(k) + \tilde{\alpha}_{\mathrm{b}}(k) = \Delta\tilde{\alpha}(k) + \tilde{\alpha}_{\mathrm{b}}(0) \tag{35}$$

where we ignore the k dependence of the background part $\tilde{\alpha}_{\mathrm{b}}(k)$ and consider it in the hydrodynamic limit $\tilde{\alpha}_{\mathrm{b}}(k) = \tilde{\alpha}_{\mathrm{b}}(0) = \tilde{\alpha}_{\mathrm{b}}$. Than Eq. (30), with account of Eqs. (29) and (34), reads

$$\Delta\tilde{\alpha} = \frac{k_{\mathrm{B}} T \rho}{6\pi\eta\xi} \left(\frac{\partial x}{\partial \mu}\right)_{P,T} \Omega_{x}(q_{D}\xi) \tag{36}$$

where

$$\Omega_{x}(q_{D}\xi) = \frac{2}{\pi} \int_{0}^{q_{D}\xi} \frac{dz}{\{(1+z^{2})(1 + (\tilde{\alpha}_{\mathrm{b}}/\eta)(\partial\mu/\partial x)_{P,T}\,[1 + y_{0}\sigma(z)](1+z^{2}))\}} \tag{37}$$

with

$$y_{0} = \frac{k_{\mathrm{B}} T \rho}{6\pi\eta\xi\tilde{\alpha}_{\mathrm{b}}} \left(\frac{\partial x}{\partial \mu}\right)_{P,T} \tag{38}$$

The integral in Eq. (37) can be evaluated rigorously only numerically. However, in the critical region at $k = q_{D} \gg \xi^{-1}$ a reasonable approximation for the crossover function $\Omega_{x}(q_{D}\xi)$ can be obtained if we put into Eq. (37) $\sigma(z) \equiv 0$. Integration of Eq. (37) in this case yields

$$\Omega_{x}(q_{D}\xi) = \frac{2}{\pi}\left[\arctan(q_{D}\xi) - \frac{1}{\sqrt{1 + y_{D} q_{D}\xi}} \arctan\frac{q_{D}\xi}{\sqrt{1 + y_{D} q_{D}\xi}}\right] \tag{39}$$

with

$$y_{D} = \frac{\eta}{\tilde{\alpha}_{\mathrm{b}} q_{D}\xi} \left(\frac{\partial x}{\partial \mu}\right)_{P,T} \tag{40}$$

At another limit $k = 0$ [$\sigma(z) \equiv 1$] integration of Eq. (37) yields the same crossover function as specified by Eq. (39) but with the parameter

$$y_{D} = \frac{6\pi\eta^{2}}{k_{\mathrm{B}} T \rho q_{D}(1 + y_{0}^{-1})} \tag{41}$$

which in the limit $y_{0} \ll 1$ also corresponds to Eq. (40). At a constant value $k = k_{D}$ in the intermediate region $0 < k_{D} < q_{D}$, integration of Eq. (37) yields

$$y_{D} = \frac{6\pi\eta^{2}}{k_{\mathrm{B}} T \rho q_{D}(\sigma_{0} + y_{0}^{-1})} \tag{42}$$

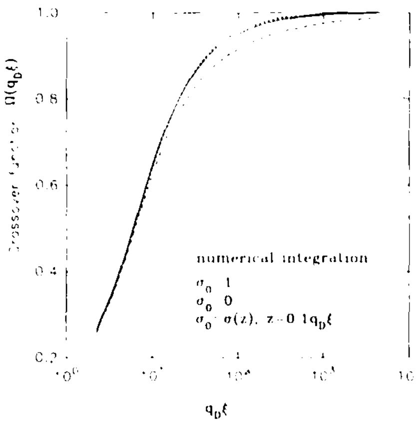

Fig. 2. Crossover function Ω for the transport coefficient $\Delta\tilde{\chi}$. The solid curve corresponds to numerical integration of Eq. (37), the long-dashed curve represents the crossover function defined by Eq. (39) with parameter y_D as defined by Eq. (41), the dotted curve represents values calculated with y_D defined by Eq. (40), and the dashed curve corresponds to the solution (42) with $k_D = 0.1q_D$.

where $\sigma_0 = \sigma(k_D\xi)$, and $\sigma(k_D\xi)$ is the same function as defined by Eq. (34) but with $z = k_D\xi$. At $k_D \gg \xi^{-1}$, $\sigma_0 = 0$ and Eq. (42) corresponds to the solution defined by Eq. (40). At $k_D \ll \xi^{-1}$ the function $\sigma_0 = 1$, and Eq. (42) transforms to Eq. (41). For the real k-dependent dynamical function $\sigma(k\xi)$ the numerical estimates of integral (37) show that the parameter k_D in Eq. (42) can be fixed at a constant value $k_D = 0.1q_D$. A comparison of the numerical calculation of integral (37) with the analytical solution defined by Eqs. (39) and (42) is shown in Fig. 2. As one can see in the wide range of the parameter $q_D\xi$ both solutions, defined by Eqs. (39) and (42) with $\sigma_0 = \sigma(0.1q_D\xi)$ and obtained by numerical integration, give practically the same crossover functions. Asymptotically close to the critical point $q_D\xi \gg 1$, the singular part of the transport coefficient is much bigger than the regular (background) one ($y_0 \gg 1$, $y_D \approx 1$), all crossover functions approach unity, and Eq. (36) in the critical limit corresponds exactly to the asymptotic solution (9). Far away from the critical point $q_D\xi \ll 1$, and the crossover function $\Omega_\chi \to 0$. Thus a reasonable approximation for the crossover function $\Omega_\chi(q_D\xi)$ can be obtained even if we ignore the k-dependence of the dynamical function $\sigma(z)$ in Eq. (37) and consider it only at the constant value of the wave number $k = k_D = 0.1q_D$.

4. THE CROSSOVER FUNCTION FOR THE TRANSPORT COEFFICIENTS $\tilde{\beta}$ AND $\tilde{\gamma}$

The essential step in applying the decoupled-mode method to calculating transport coefficients is the determination of the expression for the fluctuating current in terms of the basic fields. To present the coefficients $\Delta\tilde{\beta}$ and $\Delta\tilde{\gamma}$ in a similar form we should rewrite the correlation functions of the concentration and the entropy through the order-parameter correlation functions. For this purpose it is convenient to represent the ordering field h in Eq. (23) as

$$h = \mu - \mu_c = \left(\frac{\partial \mu}{\partial T}\right)_{P,x} (T - T_c) \tag{43}$$

The local entropy becomes

$$S(\vec{r}, t) = -\frac{a}{2T_c}\varphi^2(\vec{r}, t) + \left(\frac{\partial \mu}{\partial T}\right)_{P,x} \varphi(\vec{r}, t) \tag{44}$$

that corresponds exactly to the scalar extra field $q(\vec{r})$ introduced by Siggia et al. in their renormalization-group treatment [21]. The corresponding expressions for the correlation functions $\langle \delta x\, \delta S\rangle$ and $\langle \delta S\, \delta S\rangle$ read

$$\langle \delta x(0, 0)\, \delta S(\vec{r}, t)\rangle = \left(\frac{\partial \mu}{\partial T}\right)_{P,x} \langle \delta\varphi(0, 0)\, \delta\varphi(\vec{r}, t)\rangle \tag{45}$$

$$\begin{aligned}\langle \delta S(0, 0)\, \delta S(\vec{r}, t)\rangle = {} & \left(\frac{\partial \mu}{\partial T}\right)^2_{P,x} \langle \delta\varphi(0, 0)\, \delta\varphi(\vec{r}, t)\rangle \\ & + \frac{a^2}{4T_c^2} \langle \delta\varphi^2(0, 0)\, \delta\varphi^2(\vec{r}, t)\rangle\end{aligned} \tag{46}$$

Substitution of Eq. (45) into Eq. (16) yields

$$\Delta\tilde{\beta} = \frac{k_B T\rho}{6\pi\eta\xi} \left(\frac{\partial x}{\partial T}\right)_{P,\mu} \Omega_\beta(q_D\xi) \tag{47}$$

where the crossover function Ω_β coincides with the crossover function for $\Delta\tilde{\alpha}$:

$$\Omega_\beta(q_D\xi) = \Omega_\alpha(q_D\xi) \tag{48}$$

With account of Eq. (46), Eq. (17) for $\Delta\tilde{\gamma}$ takes the form

$$\Delta\tilde{\gamma} = \frac{k_B T^2\rho}{6\pi\eta\xi} \left(\frac{\partial \mu}{\partial T}\right)^2_{P,x} \left(\frac{\partial x}{\partial \mu}\right)_{P,T} \Omega_\gamma(q_D\xi) + \frac{k_B T\rho C_{P,x}}{6\pi\eta\xi} \Omega_{1\gamma}(q_D\xi) \tag{49}$$

where $\Omega_{\gamma}(q_D\xi) \sim \langle \delta\varphi \, \delta\varphi \rangle$ and, as in the previous case, coincides with the crossover function for $\Delta\tilde{\alpha}$:

$$\Omega_{\gamma}(q_D\xi) = \Omega_{\alpha}(q_D\xi) \tag{50}$$

A direct calculation of the crossover function $\Omega_{1\gamma}(q_D\xi) \sim \langle \delta\varphi^2 \, \delta\varphi^2 \rangle$ results in a slight logarithmic divergence, $\Omega_{1\gamma} \sim \ln(q_D\xi)$. The reason for this nonphysical divergence arises from the fact that the correlation function $\langle \delta\varphi^2 \, \delta\varphi^2 \rangle$ is proportional to the isobaric specific heat

$$C_{P,x} \sim \int \langle \delta\varphi^2(0) \, \delta\varphi^2(\vec{r}) \rangle \, d\vec{r} \tag{51}$$

which diverges weakly as $\tau^{-\alpha}$ at a consolute critical point, whereas in the Gaussian approximation the critical exponent $\alpha = 0$. Thus within the Gaussian approximation we cannot obtain the correct result for the crossover function $\Omega_{1\gamma}$ from Eqs. (17) and (46) directly. For this purpose it is necessary to apply the renormalization-group method [2, 5, 21, 23]. However, as shown in the next section, in the limit of pure fluids $\gamma \to \lambda$, and the crossover function $\Omega_{1\gamma}(q_D\xi)$ has to transform to the crossover function of one-component fluids $\Omega(q_D\xi)$ [see Eq. (5)]. Therefore the actual form of the crossover function $\Omega_{1\gamma}(q_D\xi)$ can be derived from Eq. (2). In the hydrodynamic limit $(q \to 0)$ under the assumptions

$$C_P(k) = G(k), \quad \eta(k) = \eta(0), \quad D_T(k) = [\Delta\lambda(0)\, \sigma(k_D\xi) + \lambda_b]/\rho C_P(k) \tag{52}$$

we obtain after integration

$$\Omega(q_D\xi) = \Omega_{1\gamma}(q_D\xi) = \frac{2}{\pi}\left[\arctan(q_D\xi) - \frac{1}{\sqrt{1 + y_{1D}q_D\xi}} \arctan\frac{q_D\xi}{\sqrt{1 + y_{1D}q_D\xi}}\right] \tag{53}$$

with

$$y_{1D} = \frac{6\pi\eta^2}{k_B T\rho q_D(\sigma_0 + y_1^{-1})} \tag{54}$$

where $y_1 = k_B T\rho C_{P,x}/6\pi\eta\xi\tilde{\gamma}_b$ and $\sigma_0 = \sigma(k_D\xi)$. In the case $y_{1D} = y_D$ the crossover function $\Omega(q_D\xi)$ coincides again with the crossover function obtained for $\Omega_{\alpha}(q_D\xi)$ [see Eq. (39)]. This result may be considered additional proof of the mathematical identity of the mode-coupling calculations developed by Kawasaki [7, 9] and by Kadanoff and Swift [8] and the "decoupled-mode" approach considered in this paper. It should be noted that the crossover function $\Omega_{OS}(q_D\xi)$ [see Eq. (6)] has been obtained with simplified assumption other than $\Omega_{1\gamma}(q_D\xi)$. Therefore the forms of $\Omega_{1\gamma}$ and Ω_{OS} are different. A comparison of these crossover functions is shown in Fig. 3 (for simplicity we consider $y_{1D} \simeq y_D \simeq 6\pi\eta^2/k_B T\rho q_D$ as a new system-dependent parameter). One can see that the crossover function Ω_{OS}, unlike the crossover function $\Omega_{1\gamma}$, has a maximum at temperatures $\tau \approx 10^{-1}$. This maximum arises from the second term on the right-hand side of Eq. (6) (term $\sim \xi C_v/C_P$), which is a product of the integration of Eq. (2) at assumption $C_P(k) = G(k) + C_v(0)$ and $D_T(k) = 0$, unlike assumption (52) accepted in this paper. In the nearest vicinity of the critical point of a binary mixture $C_v \sim C_{v,x} \simeq \text{const}$, $C_P \sim C_{P,x} \propto \tau^{-\alpha}$, $\xi \propto \tau^{-\nu}$ (see, e.g., Refs. 24 and 25) and this term at $\tau \to 0$ produces an unphysical divergence of the crossover function $\Omega_{OS} \to \infty$, as our crossover function $\Omega_{1\gamma} \to 1$. A more rigorous solution of the mode-coupling integral (2) obtained by Olchowy and Sengers [12] gives a better representation of the crossover function $\Omega(q_D\xi)$ than the simplified model defined by Eq. (6), but that solution is much more complicated than the simple approximation (53) obtained in this paper.

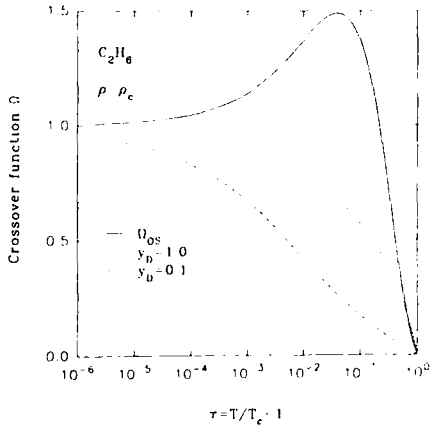

Fig. 3. Crossover function $\Omega(q_D\xi)$ for the thermal conductivity of ethane along the critical isochore. The dashed curves are generated by Eq. (53), and the solid curve represents the simplified approximation of Olchowy and Sengers [13]. The thermodynamic properties were calculated from an asymmetric scaled equation [26].

Finally, the crossover expressions for the kinetic coefficients of a binary mixture can be written in the form

$$\tilde{\alpha} = \frac{k_{\mathrm{B}} T\rho}{6\pi\eta\xi}\left(\frac{\partial x}{\partial\mu}\right)_{P,T} \Omega_x(q_D\xi) + \tilde{\alpha}_{\mathrm{b}} \tag{55}$$

$$\tilde{\beta} = \frac{k_{\mathrm{B}} T\rho}{6\pi\eta\xi}\left(\frac{\partial x}{\partial T}\right)_{P,\mu} \Omega_x(q_D\xi) + \tilde{\beta}_{\mathrm{b}} \tag{56}$$

$$\tilde{\gamma} = \frac{k_{\mathrm{B}} T^2\rho}{6\pi\eta\xi}\left(\frac{\partial x}{\partial\mu}\right)_{P,T}\left(\frac{\partial\mu}{\partial T}\right)^2_{P,x} \Omega_x(q_D\xi) + \frac{k_{\mathrm{B}} T\rho C_{P,x}}{6\pi\eta\xi}\,\Omega(q_D\xi) + \tilde{\gamma}_{\mathrm{b}} \tag{57}$$

where the crossover functions $\Omega_x(q_D\xi)$ and $\Omega(q_D\xi)$ are given by Eqs. (39), (42), and (53).

5. CROSSOVER BEHAVIOR OF THE THERMAL CONDUCTIVITY

The thermal conductivity of the mixture λ is defined by the equations

$$\vec{J}_{\mathrm{d}} = 0, \qquad \vec{J}_{\mathrm{q}} = -\lambda\nabla T \tag{58}$$

which, according to Eqs. (7) and (8), lead to the following relation between λ and the kinetic coefficients $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$ [16]:

$$\lambda = \tilde{\gamma} - T(\tilde{\beta}^2/\tilde{\alpha}) \tag{59}$$

Substituting crossover equations, Eqs. (55)–(57), for the kinetic coefficients into Eq. (59), we obtain

$$\lambda = \frac{k_{\mathrm{B}} T\rho C_{P,x}}{6\pi\eta\xi}\,\Omega(q_D\xi) + \tilde{\alpha}_{\mathrm{b}}\mu_T^2 T Q(y) + \tilde{\gamma}_{\mathrm{b}} \tag{60}$$

where the crossover function $\Omega_x(q_D\xi)$ now appears only in the argument

$$y = \Delta\tilde{\alpha}/\tilde{\alpha}_{\mathrm{b}} = \frac{k_{\mathrm{B}} T\rho}{6\pi\eta\xi\tilde{\alpha}_{\mathrm{b}}}\left(\frac{\partial x}{\partial\mu}\right)_{P,T} \Omega_x(q_D\xi) \tag{61}$$

of the new crossover function

$$Q(y) = \frac{y(1+2y^*) - (y^*)^2}{1+y} \tag{62}$$

In Eqs. (60) and (62) we have introduced the notation $\mu_T = (\partial\mu/\partial T)_{P,x}$ and $y^* = \tilde{\beta}_{\mathrm{b}}/\mu_T\tilde{\alpha}_{\mathrm{b}}$. So the behavior of the thermal conductivity of a binary mixture in the critical region is determined by the crossover function $Q(y)$.

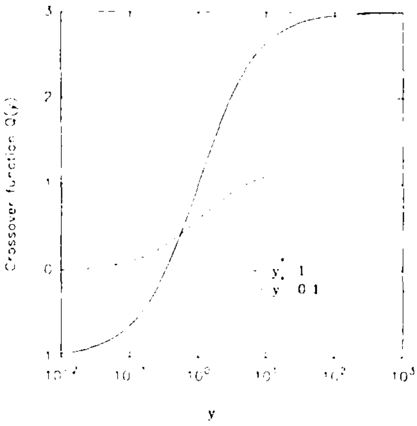

Fig. 4. Crossover function $Q(y)$ generated by Eq. (62) for two values of the parameter y^*.

A plot of this function at two values of y^* is shown in Fig. 4. Far from the critical point when $y \ll 1$ $(q_D\xi \ll 1,\ \Omega \ll 1,\ \Omega_x \ll 1)$

$$Q(y) \simeq -(y^*)^2 + (1+y^*)^2\, y \tag{63}$$

and the thermal conductivity tends to its regular (background) part

$$\lambda_b = \tilde{\gamma}_b - \tilde{\alpha}_b T \mu_T^2 (y^*)^2 = \tilde{\gamma}_b - T\tilde{\beta}_b^2/\tilde{\alpha}_b \tag{64}$$

Asymptotically close to the critical point at $y \gg 1$ $(q_D\xi \gg 1,\ \Omega \cong \Omega_x \cong 1)$

$$Q(y) \simeq 1 + 2y^* - (1+y^*)^2/y \tag{65}$$

and the thermal conductivity reads

$$\lambda \simeq \frac{k_B T \rho C_{P,x}}{6\pi\eta\xi} - \tilde{\alpha}_b (1+y^*)^2\, T\frac{\mu_T^2}{y} + \lambda_{cb} \tag{66}$$

where the critical background

$$\lambda_{cb} = \lambda_b + T\mu_T^2 \tilde{\alpha}_b (1+y^*)^2 \tag{67}$$

is not equal to the regular part λ_b.[3] The consolute point of a binary mixture is isomorphic to the critical point of a one-component fluid and the specific heat $C_{P,x}$ has the same behavior as the specific heat C_v of a pure fluid $[C_{P,x} \sim \tau^{-\alpha}(P)$, where $\tau(P) = T/T_c(P) - 1]$. This means that the

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[3] For a mixture near the plaint point this has also been shown by Mostert and Sengers [27].

first term on the right-hand side of Eq. (66) in the consolute point is equal to zero and in the intermediate region $y \simeq 1$, and both quantities Q and λ demonstrate the crossover from the regular background (63) and (64) to the critical background (65) and (67).

Equations (53), (60), and (62) have been obtained at the consolute point. Nevertheless, according to the isomorphism hypothesis [20], which is confirmed by direct mode-coupling calculations [17], we may extend them to a binary mixture near the liquid–vapor critical point, but in this case the isomorphic path $\mu = \text{const}$ does not coincide with the experimental path $x = \text{const}$, and the derivatives $(\partial x/\partial \mu)_{P,T}$, $(\partial \mu/\partial T)_{P,x}$ and the specific heat $C_{P,x}$ are renormalized. In accordance with the results of a previous analysis carried out by Anisimov and Kiselev [24, 25], the connection between the isomorphic variable $\tau(\mu) = T/T_c(\mu) - 1$ and the experimental variable $\tau(x) = T/T_c(x) - 1$ along the critical isochore is not analytic,

$$\tau^{1-\alpha}(\mu)[1 + \tau^{\alpha}(\mu)/X_A] = \tau(x)/X_A \tag{68}$$

where the parameter

$$X_A \cong \frac{A_0 k_B T_c}{(1-\alpha)} \frac{dx}{d\mu_c} \left(\frac{1}{T_c} \frac{dT_c}{dx} \right)^2 \tag{69}$$

is equal to zero at the critical points of the pure components. Far from the critical point such that

$$\tau(x) \gg X_A^{1/\alpha} \tag{70}$$

$$\tau(\mu) \simeq \tau(x) \tag{71}$$

all isomorphic properties at $x = \text{const}$ behave as those of a one-component fluid [25],

$$C_{v,\mu} = k_B A_0 \tau^{-\alpha}(x) \tag{72}$$

$$k_B T_c \left(\frac{\partial \rho}{\partial P} \right)_{T,\mu} = \Gamma_0 \tau^{-\gamma}(x) \tag{73}$$

$$C_{P,\mu} = k_B \Gamma_0 (T_c/P_c)(dP_c/dT_c)^2 \tau^{-\gamma}(x) \tag{74}$$

$$\xi = \xi_0 \tau^{-\nu}(x) \tag{75}$$

where A_0, Γ_0, and ξ_0 are the system-dependent critical amplitudes, and α, γ, and ν are universal critical exponents. Asymptotically close to the critical point, such that

$$\tau(x) \ll X_A^{1/\alpha} \tag{76}$$

$$\tau(\mu) = [\tau(x)/X_A]^{1/(1-\alpha)} \tag{77}$$

renormalization of the critical exponents $\alpha \rightarrow \alpha/(1-\alpha)$, $\gamma \rightarrow \gamma/(1-\alpha)$, and $\nu \rightarrow \nu/(1-\alpha)$ (the "Fisher renormalization") takes place. The behavior of the nonisomorphic properties appears to be more complicated. The isochoric specific heat at a constant concentration $C_{v,x} \simeq C_{v,\mu} \propto \tau^{-\alpha}(x)$ in the region defined by inequality (70) remains finite at the critical point. At condition (76) it is a cusp with the infinite derivative [24, 25]

$$C_{v,x} = \frac{k_B A_0}{X_A}\left[1 - \frac{1}{X_A}\left(\frac{\tau(x)}{X_A}\right)^{\alpha/(1-\alpha)}\right] + (C_{v,x})_b \tag{78}$$

where $(C_{v,x})_b$ is a background specific heat. The derivative

$$\left(\frac{\partial P}{\partial \rho}\right)_{T,x} = \left(\frac{\partial P}{\partial \rho}\right)_{T,\mu} + \rho^2\left(\frac{\partial \mu}{\partial x}\right)_{T,\rho}\left(\frac{\partial x}{\partial \rho}\right)^2_{T,\mu} \tag{79}$$

at the critical isochore takes the form [25]

$$\left(\frac{\partial P}{\partial \rho}\right)_{T,x} = \frac{k_B T_c}{\Gamma_0}\tau^{\gamma}(\mu)\left[1 + \frac{X_\Gamma \tau^{-\gamma}(\mu)}{X_A \tau^{-\alpha}(\mu) + 1}\right] \tag{80}$$

Here the new characteristic parameter X_Γ reads

$$X_\Gamma \cong \frac{\Gamma_0}{k_B T_c}\frac{dx}{d\mu_c}\left[\frac{1}{\rho_c}\left(\frac{\partial P}{\partial x}\right)_{T,\mathrm{cxc}}\right]^2 \tag{81}$$

where the derivative $(\partial P/\partial x)_{T,\mathrm{cxc}}$ is taken at the condition of two-phase coexistence. Far from the critical point

$$\tau(x) \gg X_\Gamma^{1/\gamma} \tag{82}$$

the derivative $(\partial \rho/\partial P)_{T,x}$ and the specific heat $C_{P,x}$ behave as $(\partial \rho/\partial P)_T$ and C_P in one-component fluids and as $(\partial \rho/\partial P)_{T,\mu}$ and $C_{P,\mu}$ in binary mixtures [see Eqs. (73) and (74)]. Asymptotically close to the critical point at condition (76) the derivative $(\partial \rho/\partial P)_{T,x}$ and $C_{P,x}$ manifest a weak singularity with the renormalized critical exponent α,

$$k_B T_c\left(\frac{\partial \rho}{\partial P}\right)_{T,x} = \Gamma_0 \frac{X_A}{X_\Gamma}\left(\frac{\tau(x)}{X_A}\right)^{\alpha/(1-\alpha)} \tag{83}$$

$$C_{P,x} = k_B A_0\left(\frac{\tau(x)}{X_A}\right)^{-\alpha/(1-\alpha)} \tag{84}$$

Finally, in the temperature range

$$X^{1/\alpha} \ll \tau(x) \ll X_\Gamma^{1/\gamma} \tag{85}$$

$(\partial\rho/\partial P)_{T,x}$ and $C_{P,x}$ do not depend on temperature

$$\left(\frac{\partial\rho}{\partial P}\right)_{T,x} \cong \frac{\Gamma_0}{k_B T_c X_\Gamma} \tag{86}$$

$$C_{P,x} \cong \frac{k_B \Gamma_0}{X_\Gamma}\left(\frac{T_c}{P_c}\frac{dP_c}{dT_c}\right)^2 \tag{87}$$

and demonstrate the crossover from one-component-like behavior to the renormalized behavior at the edges of the temperature range.

Thus the character of the behavior of all thermodynamic properties of a binary mixture at the critical isochore $\rho = \rho_c(x)$ is determined by two "cones." A wide cone is

$$\tau(x) = X_\Gamma^{1/\gamma} \tag{88}$$

and a narrow one is

$$\tau(x) = X_A^{1/\alpha} \tag{89}$$

Outside the wide cone

$$X_\Gamma^{1/\gamma} \ll \tau(x) \ll 1 \tag{90}$$

the correlation length and isobaric specific heat at constant x of a binary mixture behaves as ξ and C_P in one-component fluids and the derivatives $(\partial x/\partial\mu)_{P,T}$ and $(\partial\mu/\partial T)_{P,x}$ for dilute solutions read

$$\left(\frac{\partial x}{\partial\mu}\right)_{P,T} \simeq \frac{x}{k_B T} \tag{91}$$

$$\left(\frac{\partial\mu}{\partial T}\right)_{P,x} \simeq k_B \ln x \tag{92}$$

It is convenient to represent the parameters X_Γ and X_A and the transport coefficients $\tilde{\alpha}_b$ and $\tilde{\beta}_b$ in the form

$$X_\Gamma = X_{0\Gamma}x(1-x), \qquad X_A = X_{0A}x(1-x) \tag{93}$$

and

$$\tilde{\alpha}_b = \tilde{\alpha}_0 x(1-x), \qquad \tilde{\beta}_b = \tilde{\beta}_0 x(1-x) \tag{94}$$

which provide the correct asymptotes for these parameters in the pure-component limit.[4] In this case the second term in Eq. (60),

$$\tilde{\alpha}_b \mu_T^2 Q(y) \simeq \tilde{\alpha}_0 x k_B^2 \ln^2 x Q(y) \tag{95}$$

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[4] In Ref. 25, $X_{0\Gamma} = \Gamma_0[(1/P_c)(dP_c/dx)]^2$, and $X_{0A} = A_0[(1/T_c)(dT_c/dx)]^2$.

and in the limit of a pure solvent ($x \to 0$), Eq. (60) transforms to Eq. (5) for the thermal conductivity of one-component fluids. Thus the crossover function $\Omega(q_D \xi)$ in the limit $x \to 0$ should transform to the crossover function in Eq. (5).

In the temperature range

$$X_A^{1/\alpha} \leqslant \tau(x) \leqslant X_\Gamma^{1/\gamma} \tag{96}$$

the correlation length reads

$$\xi = \xi_0 \tau^{-\nu}(x) \tag{97}$$

and the derivative $(\partial x/\partial \mu)_{P,T}$ is diverged as [25]

$$\left(\frac{\partial x}{\partial \mu}\right)_{P,T} \simeq \frac{x X_\Gamma}{k_B T} \tau^{-\gamma}(x) \tag{98}$$

The condition $y = 1$, in accordance with definition (61), generates a new cone,

$$\tau(x) = X_y^{1/(\gamma - \nu)} = (\kappa_0 X_\Gamma)^{1/(\gamma - \nu)} \tag{99}$$

where $\kappa_0 = \rho/6\pi\eta\tilde{\alpha}_0\xi_0$. The existence of this cone near the liquid–vapor critical point of binary mixtures has been pointed out by Onuki [28]. Outside this new (kinetic) cone $y \ll 1$ the thermal conductivity of binary mixtures demonstrates one-component-like temperature behavior. At condition (90) the parameter $y \sim \kappa_0 \tau^{\nu}(x)$ [see Eqs. (53) and (91)], the specific heat $C_{P,x} \sim \tau^{-\gamma}(x)$, and Eq. (60), as shown above, simply transforms to Eq. (5). In the temperature range

$$X_y^{1/(\gamma - \nu)} \ll \tau(x) \leqslant X_\Gamma^{1/\gamma} \tag{100}$$

the parameter

$$y \simeq X_y \tau^{-\gamma + \nu}(x) \tag{101}$$

and despite that the isobaric specific heat $C_{P,x}$ in this region does not depend on temperature [see Eq. (87)], the thermal conductivity of binary mixtures again diverges with the same power law but with another amplitude,

$$\lambda_c \simeq \tilde{\alpha}_b \mu_T^2 (1 + y^*)^2 X_y \tau^{-\gamma + \nu}(x) + \lambda_b \tag{102}$$

which corresponds to the second term on the right-hand side of Eq. (60). (The thermal conductivity λ is a sum of three terms, in accordance with Eq. (60). Both the first and the second terms may be principally divergent with some power law, or not divergent. In the temperature region defined by Eq. (100), the first term is nondivergent, but the second one diverges as $\tau(x)^{-\gamma+\nu}$ with amplitude $\tilde{\alpha}_B \mu_T^2(1+y^*)^2 X_y$. If we consider the temperature region defined by Eq. (90), the first term in λ becomes divergent with the same power law $\tau^{-\gamma+\nu}$, but with another amplitude, and the second term in Eq. (60) in this temperature region becomes nondivergent.)

Inside the cone (99) $y \gg 1$ and two different regions again exist. In the range of temperatures

$$X_A^{1/\alpha} \ll \tau(x) \ll X_y^{1/(\gamma-\nu)} \tag{103}$$

the parameter y is determined by Eq. (101), the specific heat $C_{P,x}$, as before, does not depend on temperature, and the thermal conductivity of binary mixtures tends to its critical background value as

$$\lambda \simeq \lambda_{\rm cb} - \tilde{\alpha}_{\rm b} T \mu_T^2 (1+y^*)^2 X_\Gamma^{-1} \tau^{\gamma-\nu}(x) \times \left[1 - \frac{y_0^2 \Gamma_0 k_{\rm B}^2 (T_{\rm c}/P_{\rm c})^2 (dP_{\rm c}/dT_{\rm c})^2}{x(1-x)(1+y^*)^2 \mu_T^2} \tau^{2\nu-\gamma}(x)\right] \tag{104}$$

where the critical background $\lambda_{\rm cb}$ is determined by Eq. (67). Since $2\nu-\gamma \approx 0.02 \ll 1$, the sign of the difference $\Delta\lambda_{\rm cb} = \lambda_{\rm cb} - \lambda$ is determined by the correlation of the amplitudes in the square brackets on the right-hand side of Eq. (104). Asymptotically close to the critical point at condition (76), renormalization of all critical exponents takes place, the specific heat $C_{P,x} \sim \tau^{-\alpha/1-\alpha}(x)$, and the sign of $\Delta\lambda_{\rm cb}$ is also determined by the competition of the first two terms in Eq. (104). The behavior of the thermal conductivity in the asymptotic region for a dilute-solution limit has been considered by Anisimov and Kiselev [25]. The main result of their consideration is as follows: In dilute solutions the enhancement of the thermal conductivity $\Delta\lambda_{\rm cb}$ is positive in the entire experimentally accessible region. The results of our calculations of the thermal-conductivity enhancement $\Delta\tilde{\lambda} = (\lambda - \lambda_{\rm b})/\tilde{\alpha}_0 R^2 T$ (R is the gas constant) for methane–ethane binary solutions are shown in Figs. 5–7. The thermodynamic properties were calculated from an asymmetric scaled equation [29] and an isomorphic generalization of the law of corresponding states [30, 31]. The nonuniversal parameter y^* in Eq. (62) was written as $y^* = k_{\rm B}/\mu_T$ and the kinetic parameters y_D, y_{1D}, and κ_0 were treated as system-dependent constants ($y_D = y_{1D} = 0.1$, $\kappa_0 = 1$). As one can see from these figures, at high concentrations the inequality $\lambda \leqslant \lambda_{\rm cb}$ is also valid and the crossover behavior of the thermal conductivity differs strongly from the asymptotic behavior even in the vicinity of the critical point. Thus for a description of the thermal conductivity experimental data in binary mixtures, one should use the

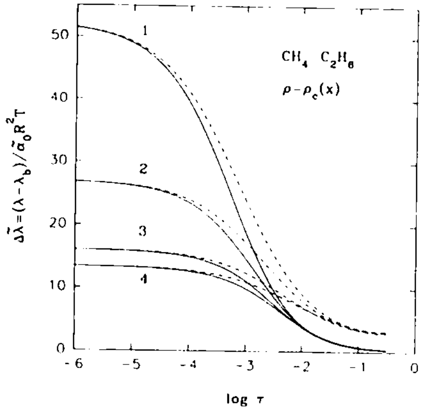

Fig. 5. The dimensionless thermal-conductivity enhancement $\Delta\bar{\lambda} = (\lambda - \lambda_b)/\bar{\alpha}_0 R^2 T$ along the critical isochore $\rho = \rho_c(x)$ for methane–ethane mixtures: $x =$ (1) 0.05, (2) 0.1, (3) 0.2, and (4) 0.5 mole fraction of ethane. The solid curves were generated by Eq. (60), and the dashed curves represent the asymptotic laws with $\Omega_\tau \equiv \Omega \equiv 1$.

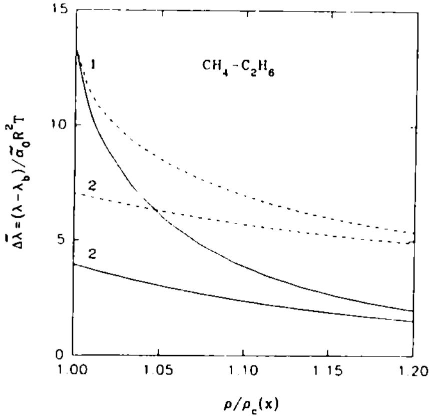

Fig. 6. The dimensionless thermal-conductivity enhancement $\Delta\bar{\lambda} = (\lambda - \lambda_b)/\bar{\alpha}_0 R^2 T$ for a methane–ethane mixture at $x = 0.5$ mole fraction of ethane along isotherms: (1) $\tau(x) = 10^{-6}$; (2) $\tau(x) = 10^{-2}$. The solid curves were generated by Eq. (60), and the dashed curves represent the asymptotic laws with $\Omega_\tau \equiv \Omega \equiv 1$.

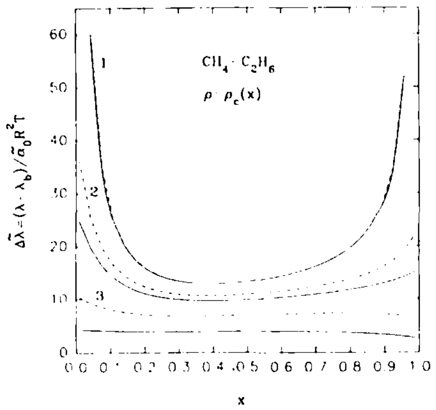

Fig. 7. The dimensionless thermal-conductivity enhancement $\Delta\tilde{\lambda} = (\lambda - \lambda_b)/\tilde{\alpha}_0 R^2 T$ at the critical density $\rho = \rho_c(x)$ for a methane–ethane mixture along isotherms: (1) $\tau(x) = 10^{-6}$; (2) $\tau(x) = 10^{-3}$; (3) $\tau(x) = 10^{-2}$. The solid curves were generated by Eq. (60), and the dashed curves represent the asymptotic laws with $\Omega_\chi \equiv \Omega \equiv 1$.

crossover model. Unfortunately we cannot provide here a direct comparison with experimental data for the thermal conductivity of the binary mixture, because the range of applicability of the isomorphic equation of state [30] is still limited and does not provide the crossover from singular thermodynamic behavior in the immediate vicinity of the critical point to regular thermodynamic behavior far from the critical point. The creation of the equation of state of binary mixtures which incorporates this crossover behavior is a separate task and is not the aim of the present paper. Nevertheless, as soon as the crossover functions $\Omega_\chi(q_D\xi)$ and $\Omega_{1\gamma}(q_D\xi)$ for the transport coefficients in the binary mixture exactly coincide with the crossover function $\Omega(q_D\xi)$ for the thermal conductivity of the one-component fluid for verification of the obtained crossover equations, we may apply them to the experimental thermal-conductivity data of pure ethane, where an extended crossover equation of state already exists [32].

6. COMPARISON WITH EXPERIMENTAL DATA FOR PURE ETHANE

To fit experimental thermal-conductivity data, one needs, in addition to the equation of state, expressions for the background transport coefficients λ_b and η_b. As noted earlier by Sengers and co-workers [6, 12–14], the excess functions $\lambda_b - \lambda_0$ and $\eta_b - \eta_0$, where λ_0 and η_0 are the transport coefficients in the dilute-gas limit, can be treated as functions of the density only, so that

$$\lambda_b = \lambda_0(T) + \sum_i \lambda_i \rho^i \tag{105}$$

$$\eta_b = \eta_0(T) + \sum_i \eta_i \rho^i \tag{106}$$

with

$$\lambda_0(T) = \sqrt{T} \Big/ \sum_j \lambda_{0j} T^{-j} \tag{107}$$

$$\eta_0(T) = \sqrt{T} \Big/ \sum_i \eta_{0i} T^{-i} \tag{108}$$

For the coefficients λ_{0j}, η_{0j}, and η_i, we adopt the same values as used by Olchowy and Sengers [12, 13], but the coefficients

$$\lambda_1 = 1.8386\ 10^{-3}, \qquad \lambda_2 = 2.9525\ 10^{-5}, \qquad \lambda_6 = -5.8296\ 10^{-9} \tag{109}$$

have been determined from a fit of the crossover equations, Eqs. (53) and (57), to the experimental data for the thermal conductivity of ethane obtained by Mostert et al. [14]. The correlation length, as generalized by Olchowy and Sengers, is

$$\xi = \xi_0(\Delta_c \tilde{\chi}/\Gamma_0)^{\nu/\gamma} \tag{110}$$

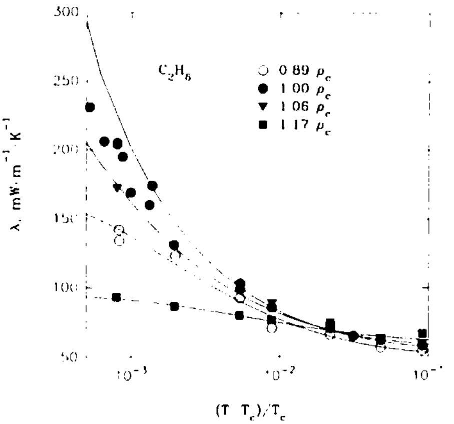

Fig. 8. The thermal conductivity of ethane as a function of temperature along isochores. The symbols indicate experimental data obtained by Mostert et al. [14] and the curves represent values calculated with the crossover model.

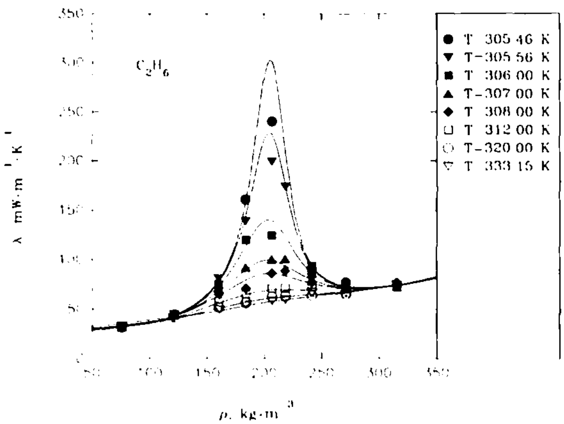

Fig. 9. The thermal conductivity of ethane as a function of the density along isotherms. The symbols indicate experimental data obtained by Mostert et al. [14] and the curves represent values calculated with the crossover model.

with

$$\Delta_c\tilde{\chi} = \tilde{\chi}(T, \rho) - \tilde{\chi}(T_r, \rho)\, T_r/T \tag{111}$$

where $\tilde{\chi} = \rho(\partial\rho/\partial P)_T P_c \rho_c^{-2}$ is a reduced isothermal compressibility and $T_r = 2T_c$ is a reference temperature. The exponents $\alpha = 0.11$, $\gamma = 1.24$, and $\nu = 0.63$ are universal, and for the system-dependent parameters ξ_0 and q_D, we adopt the values obtained by Mostert al. [14],

$$\xi_0 = 0.19\ \text{nm}; \qquad q_D^{-1} = 0.17\ \text{nm} \tag{112}$$

The result of fitting the crossover equations (53) and (57) to the experimental thermal conductivity data of Mostert et al. [14] is shown in Figs. 8 and 9. A good agreement between the calculated values of the thermal conductivity and experimental data is observed.

7. CONCLUSION

In this paper the crossover equations for the critical enhancement of the transport coefficients occurring in diffusion, heat conduction, and their cross-processes near the consolute point and the liquid–vapor critical line in fluid binary mixtures have been obtained by the decoupled-mode theory method. The crossover functions for these coefficients coincide with the crossover function for the thermal conductivity in the one-component limit.

In the critical limit the crossover expressions for the kinetic coefficients of a binary mixture reduce to the asymptotic form obtained earlier by Gorodetskii and Giterman [17] and by Mistura [18, 19] by the mode-coupling theory method. The crossover behavior of the thermal conductivity of a binary mixture has been analyzed. It is shown that the thermal conductivity of a binary mixture is nondivergent and exhibits a crossover from the critical background in the critical point to the regular background far from the critical point. The simple crossover equation for the thermal conductivity near the vapor–liquid critical line has been obtained. In the limit of pure components this equation transforms to the crossover equation for the thermal conductivity of a one-component fluid. The equation has been used for representing experimental thermal conductivity data of pure ethane. The agreement with experimental data testifies to the fact that the proposed model correctly describes the crossover behavior of the transport coefficients. For a complete description and for direct comparison with the experimental thermal-conductivity data of a binary mixture, an extended crossover equation of state for a binary mixture is needed. In this connection a new result obtained by Jin et al. [33] for the crossover equation of state of a binary mixture is very interesting.

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