

Crossover from Singular to Regular Behavior of the Transport Properties of Fluids in the Critical Region

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We present a solution of the mode-coupling equations for the dynamics of critical fluctuations which incorporates the crossover from the singular behavior of the transport properties of fluids asymptotically close to the critical point to the regular behavior of these properties far away from the critical point. Good agreement is obtained with experimental thermal diffusivity, thermal conductivity, and viscosity data for carbon dioxide at all temperatures and pressures where critical effects in these transport properties are observed.

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It is well known that the thermal conductivity and the viscosity of a fluid diverge at the critical point.¹ The singular critical behavior of the transport properties arises from the long-wavelength fluctuations of the order parameter and the other relevant hydrodynamic modes of the fluid.^{2,3} In the treatment of the behavior of transport properties in the critical region, it is customary^{1,2} to separate the thermal conductivity $\lambda = \bar{\lambda} + \Delta\lambda$ and the viscosity $\eta = \bar{\eta} + \Delta\eta$ into normal or background contributions $\bar{\lambda}$, $\bar{\eta}$ and singular critical contributions $\Delta\lambda$, $\Delta\eta$. The critical part $\Delta\lambda$ of the thermal conductivity is related to the critical part ΔD_T of the thermal diffusivity which close to the critical point satisfies a Stokes-Einstein relation of the form

$$\Delta D_T = \Delta\lambda / \rho c_p = R k_B T / 6\pi\eta\xi, \quad (1)$$

where ρ is the density, c_p the isobaric specific heat, k_B Boltzmann's constant, T the temperature, ξ the correlation

length, and $R = 1.01 \pm 0.04$ a universal amplitude. The viscosity satisfies an asymptotic power-law divergence

$$\eta = \bar{\eta}(Q\xi)^z, \quad (2)$$

where Q is a system-dependent amplitude and $z = 0.06 \pm 0.01$ a universal critical exponent.¹ However, the validity of the asymptotic equations (1) and (2) is restricted to a very small range of temperatures and densities near the critical point. In practice critical enhancements of the viscosity, and in particular of the thermal conductivity, are observed over a much wider range of temperatures and densities. In this paper we present theoretically based equations that include the nonasymptotic critical behavior and the crossover to the regular behavior of these transport properties.

The mode-coupling theory of dynamic critical phenomena² yields two coupled integral equations for the thermal diffusivity D_T and the viscosity η :

$$\Delta D_T(q) = \frac{k_B T}{(2\pi)^3 \rho} \int^{q_D} d^3k \frac{c_p(|\mathbf{q}-\mathbf{k}|)}{c_p(q)} \frac{\sin^2\theta}{k^2 \eta(k)/\rho + |\mathbf{q}-\mathbf{k}|^2 D_T(|\mathbf{q}-\mathbf{k}|)}, \quad (3)$$

$$\Delta\eta(q) = \frac{1}{2q^2} \frac{k_B T}{(2\pi)^3} \int^{q_D} d^3k c_p(k) c_p(|\mathbf{q}-\mathbf{k}|) \left[\frac{1}{c_p(k)} - \frac{1}{c_p(|\mathbf{q}-\mathbf{k}|)} \right]^2 \frac{k^2 \sin^2\theta \sin^2\phi}{k^2 D_T(k) + (\mathbf{q}-\mathbf{k})^2 D_T(|\mathbf{q}-\mathbf{k}|)}, \quad (4)$$

where q is the wave number and θ and ϕ are the polar and azimuthal angles of \mathbf{k} in a coordinate system with the polar axis in the direction of \mathbf{q} . Following earlier work of Bhattacharjee *et al.*⁴ we have neglected any frequency-dependent effects on the transport properties and retained a cutoff wave number q_D for the long-range fluctuations.

The asymptotic solutions of the mode-coupling equations originally obtained by Kawasaki⁵ correspond to $q_D \xi \rightarrow \infty$. To obtain solutions for all $q_D \xi$ we try to solve the mode-coupling equations by an iterative procedure while retaining a finite cutoff q_D .

As a first iteration we evaluate (3) by introducing into the integrand the following approximations: (a) Since $\Delta\eta \ll \eta$ we neglect the k dependence of $\eta \approx \bar{\eta}$. (b) Since

$D_T \ll \eta/\rho$ near the critical point, we neglect the term with D_T . (c) Since $c_p \gg c_v$, we take c_p to be proportional to the (symmetrized) compressibility $\chi = (\partial\rho/\partial\mu)_T$, where μ is the chemical potential. (d) For the dependence of χ on the wave number we use the Ornstein-Zernike approximation $\chi(q) = \chi(0)/(1+q^2\xi^2)$. With an infinite cutoff this procedure yields the well-known result^{5,6} $\Delta D_T(q) = (k_B T / 6\pi\eta\xi) \Omega_K(q\xi)$, where

$$\Omega_K(x) = (3/4x^2)[1 + x^2 + (x^3 - x^{-1}) \arctan x]$$

is commonly referred to as the Kawasaki function. With a finite cutoff, the integral (3) cannot be evaluated analytically, but we have found that the numerical solution is well represented for $q\xi \leq q_D\xi$ by an analytic ap-

proximant of the form⁷

$$\Delta D_T(q) = \frac{k_B T}{6\pi\eta\xi} \Omega_K(q\xi; q_D\xi), \quad (5)$$

with

$$\Omega_K(x; x_D) = \frac{3}{4} (1+x^2)^{1/2} [y_D + y_\delta (1+x^2)^{1/2}].$$

Here $x = q\xi$, $x_D = q_D\xi$, while the functions y_D and y_δ are given in Table I.

In the second iteration we retain approximations (a) and (d), but substitute in the integrands of (3) and (4) $D_T(q) = \Delta D_T(q) + \bar{D}_T(q)$, where $\bar{D}_T(q) = \bar{\lambda}/\rho c_p(q)$, while $\Delta D_T(q)$ is given by (5). For $c_p(q)$ we take

$$\rho c_p(q) = \rho c_v(q) + T \rho^{-2} (\partial P / \partial T)_\rho^2 \chi(q),$$

but neglect the wave-number dependence of the isochoric specific heat c_v . In the limit $q \rightarrow 0$ the mode-coupling integrals then become

$$\Delta D_T = \frac{k_B T}{6\pi\eta\xi} \frac{2}{\pi(1+y_\gamma)} \int_0^{y_D} dy \frac{(\cos^2 y + y_\gamma)^2}{\cos^4 y + y_\alpha y_D \cos^3 y + (y_\gamma + y_\beta + y_\alpha y_\delta) \cos^2 y + y_\gamma y_\alpha y_D \cos y + y_\gamma y_\alpha y_\delta}, \quad (6)$$

$$\Delta \eta = \bar{\eta} \frac{4}{15\pi y_D} \int_0^{y_D} dy \frac{(\cos^2 y - 1)^2 \cos^4 y}{(\cos^2 y + y_\gamma)(\cos^3 y + y_\eta \cos^2 y + y_\gamma \cos y + y_\nu)}, \quad (7)$$

TABLE I. Crossover functions for λ and η .

| | |
|--|---|
| $y_\alpha = \rho k_B T / 8\pi\eta^2 \xi$; $y_\beta = \bar{\lambda} / \bar{\eta} (c_p - c_v)$; $y_\gamma = c_v / (c_p - c_v)$ $y_D = \arctg x_D$; $y_\delta = [\arctg(x_D / (1+x_D^2)^{1/2}) - y_D] / (1+x_D^2)^{1/2}$ | |
| $\Omega(\{y_i\}) = \frac{2}{\pi} \frac{1}{1+y_\gamma} \left[y_D - \sum_{i=1}^4 Y_i \cdot F(z_i, y_D) \right]$ $\Omega_0 = \frac{[1 - \exp[-1/(1/q_D \xi + (q_D \xi \cdot \rho c / \rho)^2 / 3)]]}{\frac{\pi}{2} \cdot (1 + y_\alpha (y_D + y_\delta) + y_\beta (1+y_\gamma)^{-1})}$ | $\vec{y} = \begin{bmatrix} Y_1 \\ Y_2 \\ Y_3 \\ Y_4 \end{bmatrix}$ $\vec{y} = \underline{\underline{W}}^{-1} \vec{x}$ |
| $\underline{\underline{W}} = [w_{ij}]$; $w_{11} = 1$ $w_{2i} = \sum_{j=1}^4 z_j \cdot (1 - \delta_{ij})$; $w_{4i} = [\sum_{j=1}^4 z_j] / z_i$ $w_{3i} = -z_i \cdot w_{2i} + \frac{1}{2} \sum_{j,k=1}^4 z_j z_k \cdot (1 - \delta_{jk})$ | $\vec{x} = \begin{bmatrix} y_D y_\alpha \\ y_\beta - y_\gamma + y_\alpha y_\delta \\ y_\gamma y_\alpha y_D \\ y_\gamma y_\alpha y_\delta - y_\gamma^2 \end{bmatrix}$ |
| $\prod_{i=1}^4 (z + z_i) = z^4 + a_3 z^3 + a_2 z^2 + a_1 z + a_0 = 0$ $a_3 = y_D y_\alpha$; $a_2 = y_\gamma + y_\beta + y_\alpha y_\delta$; $a_1 = y_\gamma y_\alpha y_D$; $a_0 = y_\gamma y_\alpha y_\delta$ | |
| $H(\{y_i\}) = h(\{y_i\}) + \sum_{i=1}^3 N_i \cdot F(v_i, y_D)$ $h(\{y_i\}) = (3y_\gamma y_\eta + 3y_\eta / 2 - y_\nu^3 - y_\nu) y_D$ $+ (y_\eta^2 - 2y_\gamma - 5/4) \sin y_D - y_\eta \sin 2y_D / 4 + \sin 3y_D / 12$ $+ \frac{(y_\gamma (1+y_\gamma))^{3/2}}{(y_\nu - y_\gamma y_\eta)} \arctg \left[\frac{y_\gamma / (1+y_\gamma)}{1} \right]^{1/2} \tan y_D$ | $\vec{n} = \begin{bmatrix} N_1 \\ N_2 \\ N_3 \end{bmatrix}$ $\vec{n} = \underline{\underline{M}}^{-1} \vec{p}$ $\underline{\underline{M}} = [M_{ij}]$ $M_{11} = 1$ |
| $\prod_{i=1}^3 (v + v_i) = v^3 + y_\eta v^2 + y_\gamma v + y_\nu = 0$ $y_\eta = (y_\delta + y_\beta / y_\alpha) / y_D$; $y_\nu = y_\gamma y_\delta / y_D$ | $M_{2i} = -v_i + \sum_{j=1}^3 v_j$ $M_{3i} = [\prod_{j=1}^3 v_j] / v_i$ |
| $\vec{p} = \begin{bmatrix} y_\eta^4 - 4y_\eta^2 y_\gamma - 2y_\eta^2 + 2y_\eta y_\nu + 3y_\gamma^2 + 4y_\gamma + 1 \\ (y_\eta y_\gamma - y_\nu) (y_\eta^2 - 3y_\gamma - 2) + y_\gamma^2 (1+y_\gamma)^2 / (y_\eta y_\gamma - y_\nu) \\ y_\eta y_\nu (y_\eta^2 - 3y_\gamma - 2) + y_\nu^2 + y_\nu y_\gamma (1+y_\gamma)^2 / (y_\eta y_\gamma - y_\nu) \end{bmatrix}$ | |
| $F(r, s) = \frac{1}{(1-r^2)^{1/2}} \log \left[\frac{1+r+(1-r^2)^{1/2} \tan(s/2)}{1+r-(1-r^2)^{1/2} \tan(s/2)} \right]$ | |

with the functions y_α , y_β , y_γ , y_η , and y_ν as defined in Table I. In this form the mode-coupling integrals can be evaluated analytically.

For the thermal diffusivity we obtain

$$\Delta D_T = \frac{\Delta \lambda}{\rho c_p} = \frac{R k_B T}{6\pi\eta\xi} [\Omega(\{y_i\}) - \Omega_0], \quad (8)$$

with the functions $\Omega(\{y_i\})$ and Ω_0 given in Table I. The presence of the subtracted term Ω_0 in (8) requires an explanation. Far away from the critical point the mode-coupling integral (3) yields a small but finite result as part of the so-called long-time-tail contributions to the transport properties of dense fluids.⁸ In order to identify $\bar{\lambda}$ with the experimentally observed thermal conductivity far away from the critical point, this part needs to be incorporated into the background $\bar{\lambda}$ (or \bar{D}_T) and to be subtracted from ΔD_T .

For the viscosity we obtain

$$\eta = \bar{\eta} \exp[zH(\{y_i\})], \quad (9)$$

with the function $H(\{y_i\})$ also defined in Table I. The derivation of (9) involves an exponentiation^{4,9} to reconcile the predictions from the mode-coupling theory for $\Delta \eta \ll \bar{\eta}$ with the asymptotic power-law behavior (2). We identify z in (9) with the critical exponent in (2), although strictly speaking we find $z = 4/15\pi y_D$ which only assumes a universal value $8/15\pi^2$ in the limit $q_D \xi \rightarrow \infty$.

We have made a comparison of the crossover formulas (8) and (9) with experimental data for the transport properties of carbon dioxide. For this purpose we have used the universal values $R = 1.01$ and $z = 0.06$ quoted earlier. The thermodynamic properties have been calculated from the scaled equation of Albright *et al.*¹⁰ in the near-critical region and from the equation of Ely, Magee, and Haynes¹¹ elsewhere. We estimate the correlation length ξ by relating it to the critical part $\Delta \bar{\chi}$ of the dimensionless compressibility^{7,12}:

$$\xi = \xi_0 (\Delta \bar{\chi} / \Gamma)^{1/\gamma},$$

with $\Delta \bar{\chi} = \bar{\chi}(T, \rho) - \bar{\chi}(T_c, \rho) T_r / T$, where $\bar{\chi} = \chi P_c / \rho_c^2$ and

where the background compressibility $\tilde{\chi}(T, \rho)$ is related to a reference temperature $T_r = 1.5T_c$ far above the critical temperature T_c . For the critical exponents γ, ν and amplitudes Γ, ξ_0 we use $\nu = 0.63$, $\gamma = 1.2415$, $\Gamma = 0.052$ implied by the equation of Albright *et al.*,¹⁰ and $\xi_0 = 0.15$ nm as deduced from light-scattering data.¹³ To represent the background transport coefficients $\bar{\lambda}$ and $\bar{\eta}$ it is noted that the excess functions $\bar{\lambda} - \lambda_0$ and $\bar{\eta} - \eta_0$, where λ_0 and η_0 are the transport coefficients in the dilute-gas limit at the same temperature, are to a good approximation functions of the density only.^{7,14} In practice we use

$$\bar{\lambda} = \lambda_0(T) + \lambda_1 \rho + \lambda_2 \rho^2 + \lambda_5 \rho^5, \quad (10)$$

$$\bar{\eta} = \eta_0(T) + \eta_1 \rho + \eta_2 \rho^2 + \eta_4 \rho^4, \quad (11)$$

with $\lambda_1 = 3.09896 \times 10^{-5}$, $\lambda_2 = 5.57821 \times 10^{-8}$, $\lambda_5 = 2.59898 \times 10^{-17}$, and $\eta_1 = 5.5934 \times 10^{-9}$, $\eta_2 = 6.1757 \times 10^{-11}$, $\eta_4 = 2.643 \times 10^{-17}$ with λ in watts per meter per kelvin, η in pascals per second, and ρ in kilograms per cubic meter. The cutoff q_D in our crossover formulas (8) and (9) is treated as an adjustable parameter determined from the experimental thermal conductivity data.¹⁵ We find $q_D^{-1} = 0.23$ nm which is indeed a microscopic distance.

In Fig. 1 we present a comparison of our crossover formula (8) with the thermal diffusivity data obtained by Becker and Grigull¹⁶ and with the values deduced from the thermal conductivity data of Michels, Sengers, and van der Gulik.¹⁵ The coefficients in Eq. (10) for the background thermal conductivity were determined from

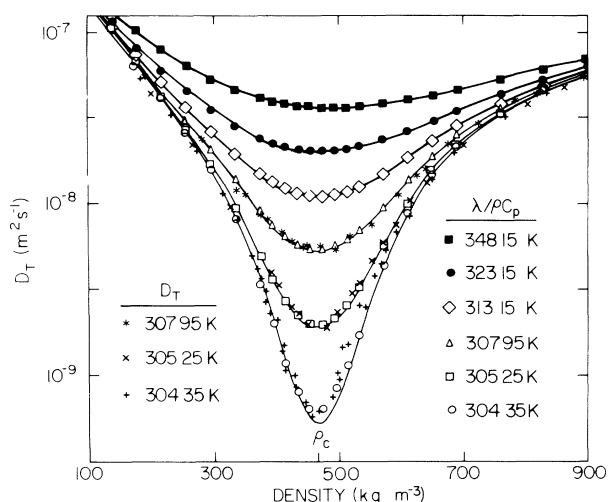


FIG. 1. The thermal diffusivity of carbon dioxide in the critical region as a function of density at various temperatures. The experimental data for the thermal diffusivity D_T are those measured by Becker and Grigull (Ref. 16) and the thermal conductivity data λ are those measured by Michels, Sengers, and van der Gulik (Ref. 15). The solid curves represent the values calculated from (8).

the experimental thermal conductivity of Michels, Sengers, and van der Gulik¹⁵ at $\rho \leq 10$ kg/m³ and $\rho \geq 1000$ kg/m³ and from the data of Le Neindre *et al.*¹⁷ at temperatures above 450 K where any critical enhancement of the thermal conductivity can be neglected. Equation (10) represents these thermal-conductivity data outside the critical region with a standard deviation $\sigma = 0.7\%$.

Viscosity measurements near the critical point of CO₂ have been reported by Iwasaki and Takahashi¹⁸ and by Bruschi and Torzo,¹⁹ but the data sets are mutually inconsistent.⁷ We have accepted the data of Iwasaki and Takahashi as the more reliable, since at lower densities they are in excellent agreement with independent viscosity measurements of Kestin, Korfali, and Sengers.²⁰ Extrapolation of the available experimental viscosity data²¹ outside the critical region to obtain the background viscosity cannot be done with an accuracy better than 2%. Since the critical viscosity enhancement is very weak, a more accurate determination of the background viscosity $\bar{\eta}$ is desirable. In the case of the viscosity we therefore reversed the procedure. Assuming that (11) is appropriate in the small temperature range 298.15 K $\leq T \leq 304.95$ K where an anomalous behavior of the viscosity is observed, we subtracted the predicted critical viscosity enhancement $\Delta\eta$ from the experimental viscosity data of Iwasaki and Takahashi¹⁸ and Kestin, Korfali, and Sengers²⁰ and represented the background viscosity data thus obtained in terms of (11). In the temperature range mentioned our equation for $\bar{\eta}$ represents the $\bar{\eta}$ from Iwasaki and Takahashi with a standard deviation σ less than 0.3% and the data of Kestin, Korfali, and Sengers with $\sigma = 0.7\%$. In Fig. 2 we present a compar-

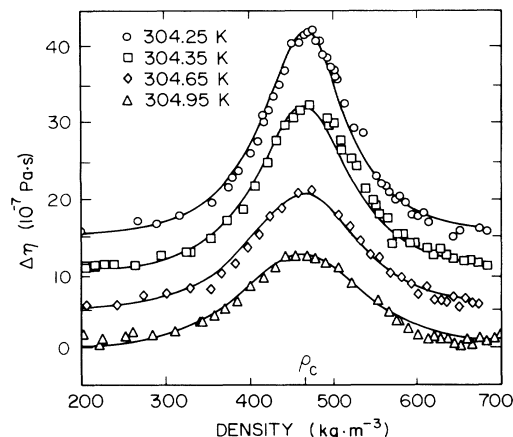


FIG. 2. The critical viscosity enhancement $\Delta\eta$ of carbon dioxide in the critical region as a function of density at various temperatures. The data points are deduced from the measurements of Iwasaki and Takahashi (Ref. 18) and the solid curves represent the values calculated from (9). To separate the isotherms the values of $\Delta\eta \times 10^7$ at 304.65, 304.35, and 304.25 K have been displaced by +5, +10, and 15 Pa·s, respectively.

ison of our crossover equation (9) with the critical viscosity $\Delta\eta$ deduced from the data of Iwasaki and Takahashi. The critical enhancement in the viscosity is quite small and to obtain adequate resolution we give in Fig. 2 a comparison with the critical enhancement $\Delta\eta$ directly.

From Figs. 1 and 2 we conclude that we have obtained crossover formulas which represent the thermal diffusivity, thermal conductivity, and viscosity at all temperatures and densities where critical effects on these transport properties are observed.

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