International Journal of Thermophysics, Vol. 10, No. 2, 1989

A Simplified Representation for the Thermal Conductivity of Fluids in the Critical Region[1]

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A practical representation for the critical thermal conductivity enhancement is developed by incorporating a finite cutoff into the asymptotic mode-coupling integrals for the diffusivity associated with the critical fluctuations. This procedure yields a simplified approximation to a more complete nonasymptotic solution of the mode-coupling integrals obtained by us earlier. A comparison is made with thermal conductivity data for carbon dioxide, ethane, and methane.

KEY WORDS: carbon dioxide; critical phenomena; ethane; methane; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

The thermal conductivity of fluids diverges at the critical point [1]. In a recent publication we have presented a solution of the mode-coupling equations for the dynamics of critical fluctuations that describes the crossover from the singular behavior of the thermal conductivity of fluids near the critical point to the regular behavior of the thermal conductivity far away from the critical point [2]. However, the explicit form thus obtained for the crossover function for the thermal conductivity is rather complicated. It is the purpose of this paper to consider a simplified crossover function which, although less accurate than our more complete solution,

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[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

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will be adequate for practical applications. This simplified crossover function is obtained from a more approximate evaluation of the mode-coupling integrals in which the weak divergent behavior of the viscosity is neglected.

2. SIMPLIFIED EVALUATION OF THE MODE-COUPLING INTEGRAL FOR THE CRITICAL DIFFUSIVITY

To describe the enhancement of the transort properties in the critical region the thermal conductivity $\lambda = \Delta\lambda + \bar{\lambda}$ and the viscosity $\eta = \Delta\eta + \bar{\eta}$ are separated into normal or background contributions $\bar{\lambda}$, $\bar{\eta}$ and singular critical contributions $\Delta\lambda$, $\Delta\eta$ [1, 3]. The mode-coupling theory of critical dynamics yields two coupled integral equations for the singular contributions to the thermal diffusivity $D_{\mathrm{T}} = \lambda/\rho c_{\mathrm{p}}$ and the viscosity η [4]:

$$\begin{aligned} \Delta D_{\mathrm{T}}(q) &= \frac{\Delta\lambda(q)}{\rho c_{\mathrm{p}}(q)} \\ &= \frac{k_{\mathrm{B}} T}{(2\pi)^3 \rho} \int^{q_{\mathrm{D}}} d\vec{k} \left[\frac{c_{\mathrm{p}}(|\vec{q}-\vec{k}|)}{c_{\mathrm{p}}(q)} \right] \frac{\sin^2\theta}{k^2 \eta(k)/\rho + |\vec{q}-\vec{k}|^2 D_{\mathrm{T}}(|\vec{q}-\vec{k}|)} \end{aligned} \tag{1}$$

$$\begin{aligned} \Delta\eta(q) &= \frac{1}{2q^2} \frac{k_{\mathrm{B}} T}{(2\pi)^3} \int^{q_{\mathrm{D}}} d\vec{k}\, c_{\mathrm{p}}(k)\, c_{\mathrm{p}}(|\vec{q}-\vec{k}|) \\ &\quad \times \left[\frac{1}{c_{\mathrm{p}}(k)} - \frac{1}{c_{\mathrm{p}}(|\vec{q}-\vec{k}|)} \right]^2 \frac{k^2 \sin^2\theta \sin^2\phi}{k^2 D_{\mathrm{T}}(k) + |\vec{q}-\vec{k}|^2 D_{\mathrm{T}}(|\vec{q}-\vec{k}|)} \end{aligned} \tag{2}$$

where ρ is the density, c_{p} the isobaric specific heat, k_{B} Boltzmann's constant, T the temperature, and $\vec{q}$ the wave vector of the fluctuations, while θ and ϕ are the polar and azimuthal angles of $\vec{k}$ with respect to $\vec{q}$. The integrals are to be evaluated over all k up to maximum cutoff wave number $q_{\mathrm{D}} = |\vec{q}_{\mathrm{D}}|$ which is indicative of the crossover length scale [5]. In general ΔD_{T}, $\Delta\lambda$, and $\Delta\eta$ depend on the wave number q, but here we consider only the contributions to the transport properties in the hydrodynamic limit $q \to 0$.

From an asymptotic evaluation of Eq. (1) it follows that very close to the critical point ΔD_{T} satisfies a Stokes–Einstein relation of the form

$$\Delta D_{\mathrm{T}} = \frac{\Delta\lambda}{\rho c_{\mathrm{p}}} = \frac{R k_{\mathrm{B}} T}{6\pi\eta\xi} \tag{3}$$

where ξ is the correlation length and where $R = 1.01 \pm 0.04$ is a universal amplitude [1]. However, the validity of the asymptotic behavior of Eq. (3) is restricted to a very small range of temperatures and densities near the critical point. To represent the actual behavior of the transport properties we have proposed a crossover model [2] based on a global nonasymptotic analysis of the mode-coupling integrals in Eqs. (1) and (2). This crossover model yields an adequate representation of the thermal conductivity of such fluids as carbon dioxide [2, 6], ethane [7, 8], and methane [7, 9] in the critical region.

Our crossover model, although readily programmable, is a somewhat complicated function. Therefore, we consider here the possibility of developing a simplified approximation. To obtain a simpler representation we start from the observation that the critical enhancement of the viscosity is very weak and is observed only in a small range of temperatures and densities around the critical point [1, 10]. The critical viscosity enhancement is therefore often neglected in practical applications [11, 12]. In any case there exists a large range of temperatures and densities where the critical thermal conductivity enhancement is significant but where the critical viscosity enhancement is entirely negligible. Under those conditions we may identify the viscosity $\eta(k)$ in Eq. (1) with $\eta(0) \simeq \bar{\eta}$ to obtain in the limit $q \to 0$

$$\Delta D_{\mathrm{T}} = \frac{\Delta\lambda}{\rho c_{\mathrm{p}}} = \frac{k_{\mathrm{B}} T}{(2\pi)^3 \bar{\eta}} \int^{q_{\mathrm{D}}} d\vec{k} \left[\frac{c_{\mathrm{p}}(k)}{c_{\mathrm{p}}(0)}\right] \frac{k^{-2} \sin^2\theta}{1 + D_{\mathrm{T}}(k)/\bar{\eta}\rho^{-1}} \tag{4}$$

In the near-critical region $D_{\mathrm{T}}/\bar{\eta}\rho^{-1} \ll 1$, since D_{T} vanishes at the critical point in the limit $k \to 0$. Away from the critical point the term $D_{\mathrm{T}}/\bar{\eta}\rho^{-1}$ in Eq. (4) is of order unity (and positive). Hence if we neglect the term $D_{\mathrm{T}}/\bar{\eta}\rho^{-1}$ in the integrand everywhere, we overestimate the integral. However, since $D_{\mathrm{T}}/\bar{\eta}\rho^{-1}$ never becomes much larger than unity, we can compensate to some extent for the overestimation by integrating up to a lower effective cutoff wavenumber $\bar{q}_{\mathrm{D}} < q_{\mathrm{D}}$. We thus consider as our simplified approximation

$$\Delta D_{\mathrm{T}} = \frac{\Delta\lambda}{\rho c_{\mathrm{p}}} = \frac{k_{\mathrm{B}} T}{(2\pi)^3 \bar{\eta}} \int^{\bar{q}_{\mathrm{D}}} d\vec{k} \left[\frac{c_{\mathrm{p}}(k)}{c_{\mathrm{p}}(0)}\right] k^{-2} \sin^2\theta \tag{5}$$

We note that Eq. (5) is identical to the simple mode-coupling integral originally considered by Kawasaki [13] and by Ferrell [14] except that the integration is now limited by a finite upper cutoff $\bar{q}_{\mathrm{D}}$. To evaluate Eq. (5), we note that the isobaric specific heat c_{p} is related to the isochoric specific heat c_{v} by $\rho c_{\mathrm{p}}(q) = \rho c_{\mathrm{v}}(q) + T\rho^{-2}(\partial P/\partial T)_{\rho}^{2}\,\chi(q)$, where P is the pressure and $\chi(q)$ a generalized susceptibility which, in the limit $q \to 0$, reduces to $\rho(\partial\rho/\partial P)_{\mathrm{T}}$ [15]. If we neglect the wave-number dependence of $c_{\mathrm{v}}(q)$, since c_{v} is a weakly divergent quantity, and make use of the

Ornstein–Zernike approximation $\chi(q) = \chi(0)/(1 + q^2\xi^2)$ [15], we obtain the simplified crossover function

$$\Delta D_{\mathrm{T}} = \frac{\Delta\lambda}{\rho c_{\mathrm{p}}} = \frac{R k_{\mathrm{B}} T}{6\pi\bar{\eta}\xi} (\bar{\Omega} - \bar{\Omega}_0) \tag{6}$$

with

$$\bar{\Omega} = \frac{2}{\pi}\left[\left(\frac{c_{\mathrm{p}} - c_{\mathrm{v}}}{c_{\mathrm{p}}}\right) \operatorname{arctg}(\bar{q}_{\mathrm{D}}\xi) + \frac{c_{\mathrm{v}}}{c_{\mathrm{p}}} \bar{q}_{\mathrm{D}}\xi\right] \tag{7}$$

and

$$\bar{\Omega}_0 = \frac{2}{\pi}\left\{1 - \exp\left[-\frac{1}{(\bar{q}_{\mathrm{D}}\xi)^{-1} + (\bar{q}_{\mathrm{D}}\xi\rho_{\mathrm{c}}/\rho)^2/3}\right]\right\} \tag{8}$$

In Eq. (6) we have reintroduced the amplitude R so as to reproduce the asymptotic behavior as given by Eq. (3). The term $\bar{\Omega}_0$ subtracts a small but finite contribution far away from the critical point that arises because the same modes lead to the presence of so-called long-time tail effects on the transport properties [2]. As in our previous work [2] we relate the correlation length ξ to the dimensionless susceptibility $\tilde{\chi} = \chi P_{\mathrm{c}}/\rho_{\mathrm{c}}^2$ through

$$\xi = \xi_0(\Delta\tilde{\chi}/\Gamma)^{\nu/\gamma} \tag{9}$$

with

$$\Delta\tilde{\chi} = \tilde{\chi}(T, \rho) - \tilde{\chi}(T_{\mathrm{R}}, \rho)\, T_{\mathrm{R}}/T \tag{10}$$

Here P_{c} and ρ_{c} are the critical pressure and density, $\nu = 0.63$ and $\gamma = 1.2415$ are the critical exponents, and ξ_0 and Γ are the amplitudes of the asymptotic power laws for ξ and $\tilde{\chi}$ [15], while $T_{\mathrm{R}} = 2T_{\mathrm{c}}$ is a reference temperature far above the critical temperature T_{c}.

As for our more complete crossover model [2], this approximate crossover model depends on the equilibrium thermodynamic properties, the background transport properties $\bar{\eta}$ and $\bar{\lambda}$, and the one fluid-dependent parameter $\bar{q}_{\mathrm{D}}$. The effective cutoff $\bar{q}_{\mathrm{D}}$, as well as the original cutoff q_{D}, is in principle a function of the density and temperature [5]. In practice we treat the cutoff parameter as a constant.

3. COMPARISON WITH EXPERIMENTAL THERMAL CONDUCTIVITY DATA

We have made a comparison of the simplified crossover model given by Eq. (6) with the experimental thermal conductivity for the same fluids,

Table I. Summary of Fluid-Dependent Information

	Carbon dioxide	Ethane	Methane
T_c (K)	304.107	305.330	190.551
ρ_c ($kg \cdot m^{-3}$)	467.69	206.58	162.66
P_c (MPa)	7.3721	4.87178	4.5992
Γ	0.0520	0.0563	0.0609
ξ_0 (nm)	0.15	0.19	0.18
q_D^{-1} (nm)	0.23	0.14	0.23
$\bar{q}_D^{-1}$ (nm)	0.40	0.29	0.38
Thermodynamic properties	See Refs. 16, 17	See Refs. 7, 18	See Refs. 19, 20
$\bar{\eta}$	See Ref. 6	See Ref. 7	See Refs. 21, 22
$\bar{\lambda}$	See Ref. 6	See Ref. 7	See Ref. 9

carbon dioxide, ethane, and methane, to which we have previously applied the more complete crossover model described in Ref. 2. In this comparison we have continued to use the same information for the thermodynamic properties, the correlation length ξ and the background transport properties $\bar{\lambda}$ and $\bar{\eta}$ [7]. This information is summarized in Table I. The thermodynamic properties were calculated from a scaled equation in the near-critical region [7, 16, 19] and from a global fundamental equation outside the critical region [17, 18, 20]. The background transport properties are written as $\bar{\eta} = \eta_0 + \eta_{\text{exc}}$ and $\bar{\lambda} = \lambda_0 + \lambda_{\text{exc}}$, where η_0 and λ_0 are the viscosity and thermal conductivity in the limit $\rho \to 0$ and η_{exc} and λ_{exc} are the

Table II. Coefficients in Eq. (11) for η_{exc} and λ_{exc}[a]

	Carbon dioxide	Ethane	Methane
η_1	5.5934×10^{-3}	0	See Table III for η_{exc} of methane
η_2	6.1757×10^{-5}	6.8989×10^{-4}	
η_3	0	-7.3999×10^{-6}	
η_4	2.6430×10^{-11}	5.0970×10^{-8}	
η_5	0	-1.5825×10^{-10}	
η_6	0	1.8406×10^{-13}	
λ_1	2.4472×10^{-2}	5.2298×10^{-3}	9.5973×10^{-2}
λ_2	8.7056×10^{-5}	3.1763×10^{-4}	3.5177×10^{-4}
λ_3	-6.5480×10^{-8}	0	0
λ_4	6.5949×10^{-11}	0	1.8649×10^{-9}
λ_5	0	1.4888×10^{-12}	0

[a] ρ in $kg \cdot m^{-3}$, η_{exc} in $\mu Pa \cdot s$, and λ_{exc} in $mW \cdot m^{-1} \cdot K^{-1}$.

Table III. Coefficients in Eq. (12) for η_{exc} [a]

Methane			
i	b_i	r_i	t_i
1	22.4160	1	2
2	−18.7621	1	3
3	65.6498	2	1
4	−172.353	2	2
5	112.311	2	3
6	−25.0068	3	1
7	100.610	3	2
8	−73.8272	3	3
9	−16.1095	4	2
10	13.1929	4	3
11	1.22661	5	1

[a] $\rho_0 = 163.5\ \mathrm{kg \cdot m^{-3}}$, $T_0 = 190.77\ K$, η_{exc} in $\mu\mathrm{Pa \cdot s}$.

density-dependent excess viscosity and excess thermal conductivity [3]. In practice we represent η_{exc} and λ_{exc} by a polynomial in ρ

$$\eta_{\mathrm{exc}} = \sum_{i=1} \eta_i \rho^i, \qquad \lambda_{\mathrm{exc}} = \sum_{i=1} \lambda_i \rho^i \tag{11}$$

except for η_{exc} of methane, for which an existing Russian equation [22] of the form

$$\eta_{\mathrm{exc}} = \sum_{i=1} b_i (\rho/\rho_0)^{r_i} (T_0/T)^{t_i} \tag{12}$$

was found to be adequate. The coefficients of Eqs. (11) and (12) for the background transport properties are reproduced in Tables II and III.

The results of the comparison with thermal conductivity data for carbon dioxide [23], ethane [24, 25], and methane [24, 26] are shown in Figs. 1–3. In these figures, we have also included a comparison with our earlier, more accurate crossover model [2].

For the thermal conductivity data of Michels et al. [23] for carbon dioxide with temperatures between 305 and 350 K, the average root mean square (rms) deviation of the data from the simplified crossover model is $\sigma = 2.2\%$ with an effective cutoff $\bar{q}_D^{-1} = 0.40$ nm, versus $\sigma = 1.3\%$ with $q_D^{-1} = 0.23$ nm for the more complete crossover model. For the thermal conductivity data of Roder and Nieto de Castro [24, 25] for ethane at the 312 and 325 K isotherms, the average rms deviation from the simplified

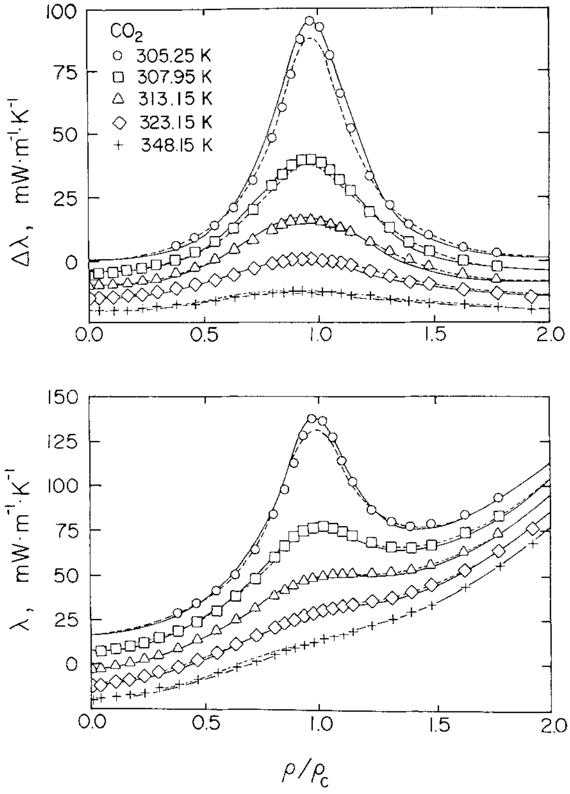

Fig. 1. The thermal conductivity of carbon dioxide in the critical region. The data are those of Michels et al. [23]. The dashed curves represent the more complete crossover model, and the solid curves the simplified approximation. The scale corresponds to the 305.25 K isotherm. The other isotherms have been shifted downward by 5 $mW \cdot m^{-1} \cdot K^{-1}$ for $\Delta\lambda$ and by 10 $mW \cdot m^{-1} \cdot K^{-1}$ for λ.

crossover model is $\sigma = 3.5\,\%$ with an effective cutoff $\bar{q}_D^{-1} = 0.29$ nm, versus $\sigma = 1.5\,\%$ with $q_D^{-1} = 0.14$ nm for the more complete crossover model. For the thermal conductivity data of Roder [24, 26] for methane at temperatures between 210 and 280 K and densities up to twice the critical density, the corresponding numbers are $\sigma = 0.73\,\%$ with an effective cutoff $\bar{q}_D^{-1} = 0.38$ nm versus $\sigma = 0.69\,\%$ with $q_D^{-1} = 0.23$ nm for the more complete crossover model. Thus the quality of the representation in terms of the simplified crossover model degrades somewhat as compared to the more complete crossover model, but not excessively.

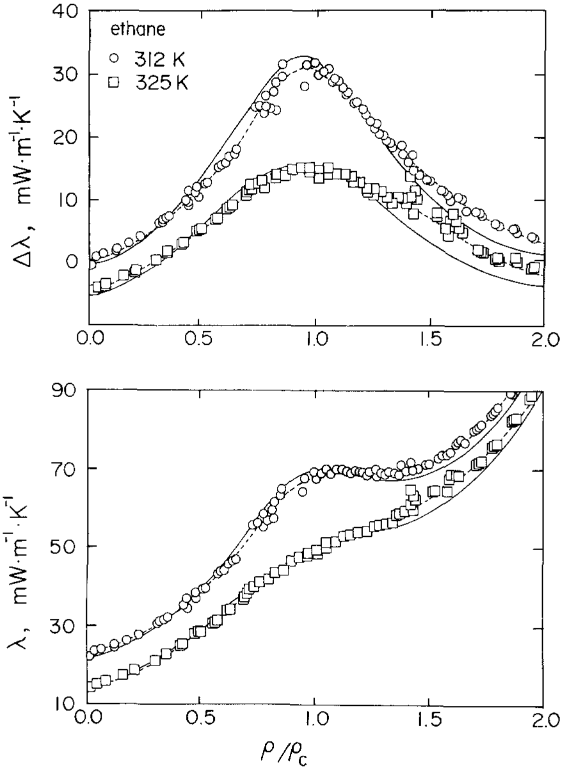

Fig. 2. The thermal conductivity of ethane in the critical region. The data are those of Roder and Nieto de Castro [24, 25]. The dashed curves represent the more complete crossover model, and the solid curves the simplified approximation. The scale corresponds to the 312 K isotherm. The other isotherms have been shifted downward by 5 mW · m^{-1} · K^{-1} for $\Delta\lambda$ and by 10 mW · m^{-1} · K^{-1} for λ.

In the past, empirical crossover functions have been used to represent the thermal conductivity of fluids in the critical region [1, 11, 12]. The simplified formulation presented in this paper is as simple as most of the empirical functions, but it has the advantage of having some theoretical basis and of containing only one fluid-dependent parameter (in addition to suitably accurate information about the thermodynamic properties and background properties).

Our simplified crossover model reproduces the Stokes–Einstein relation given by Eq. (3) asymptotically close to the critical point but with η

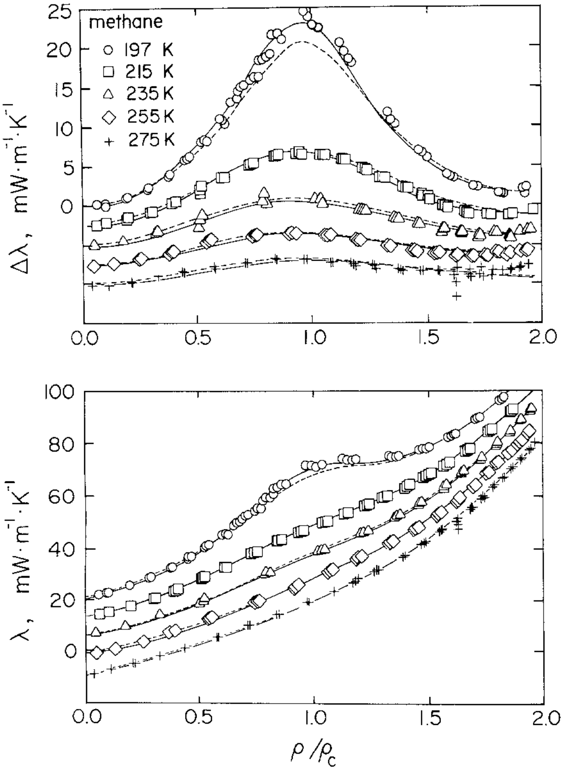

Fig. 3. The thermal conductivity of methane in the critical region. The data are those of Roder [24, 26]. The dashed curves represent the more complete crossover model, and the solid curves the simplified approximation. The scale corresponds to the 197 K isotherm. The other isotherms have been shifted downward by 2.5 mW $\cdot$ m^{-1} $\cdot$ K^{-1} for $\Delta\lambda$ and by 10 mW $\cdot$ m^{-1} $\cdot$ K^{-1} for λ.

replaced with $\bar{\eta}$. Hence, the simplified crossover model ceases to be valid at temperatures and densities so close to the critical point that the difference between the actual viscosity η and the background viscosity $\bar{\eta}$ becomes substantial.

ACKNOWLEDGMENTS

We acknowledge stimulating discussions with D. G. Friend, O. B. Tsvetkov, and W. A. Wakeham. We are also indebted to D. G. Friend for providing us with an improved global equation of state for ethane prior to publication. The research of G. A. Olchowy was supported by the Division of Chemical Sciences of the Office of Basic Energy Sciences of the U.S. Department of Energy under Grant DE-FG05-88ER13902, and the research of J. V. Sengers by the U.S. Office of Standard Reference Data under Grant 60NANB6D0657. The research has been performed under the auspices of the Subcommittee of IUPAC Commission I.2 on the Transport Properties of Fluids.

REFERENCES

1. For a review see J. V. Sengers, *Int. J. Thermophys.* **6**:203 (1985).
2. G. A. Olchowy and J. V. Sengers, *Phys. Rev. Lett.* **61**:15 (1988).
3. J. V. Sengers and P. H. Keyes, *Phys. Rev. Lett.* **26**:70 (1971).
4. K. Kawasaki, in *Phase Transitions and Critical Phenomena, Vol. 5A*, C. Domb and M. S. Green, eds. (Academic Press, New York, 1976), p. 165.
5. J. K. Bhattacharjee, R. A. Ferrell, R. S. Basu, and J. V. Sengers, *Phys. Rev. A* **24**:1469 (1981).
6. V. Vesovic, W. A. Wakeham, G. A. Olchowy, J. V. Sengers, J. T. R. Watson, and J. Millat, *J. Phys. Chem. Ref. Data* (in press).
7. G. A. Olchowy, Ph.D. thesis (University of Maryland, College Park, 1989).
8. R. Mostert, H. R. van den Berg, and P. S. van der Gulik, *Int. J. Thermophys.* **10**:409 (1989).
9. O. B. Tsvetkov, G. A. Olchowy, and J. V. Sengers (in press).
10. R. S. Basu and J. V. Sengers, in *Proceedings, 8th Symposium on Thermophysical Properties*, J. V. Sengers, ed. (American Society of Mechanical Engineers, New York, 1982), Vol. I, p. 434.
11. J. V. Sengers and J. T. R. Watson, *J. Phys. Chem. Ref. Data* **15**:1291 (1986).
12. J. C. Nieuwoudt, B. Le Neindre, R. Tufeu, and J. V. Sengers, *J. Chem. Eng. Data* **32**:1 (1987).
13. K. Kawasaki, *Ann. Phys. (N.Y.)* **61**:1 (1970).
14. R. A. Ferrell, *Phys. Rev. Lett.* **24**:1169 (1970).
15. J. V. Sengers and J. M. H. Levelt Sengers, in *Progress in Liquid Physics*, C. A. Croxton, ed. (Wiley, New York, 1978), p. 103.
16. P. C. Albright, T. J. Edwards, Z. Y. Chen, and J. V. Sengers, *J. Chem. Phys.* **87**:1717 (1987).
17. J. F. Ely, J. W. Magee, and W. M. Haynes, Research Report RR-110 (Gas Processors Association, Tulsa, Okla., 1987).
18. D. G. Friend et al., Private communication.
19. D. S. Kurumov, G. A. Olchowy, and J. V. Sengers, *Int. J. Thermophys.* **9**:73 (1988).
20. S. Angus, B. Armstrong, and K. M. de Reuck, *International Thermodynamic Tables of the Fluid State-5 Methane* (Pergamon, Oxford, 1978).
21. R. D. Trengrove and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **16**:175 (1987).
22. A. D. Koslov, V. M. Kusnezov, Y. V. Mamonov, V. I. Sukov, and A. F. Arinin, GSSSD 94-86 (Gosstandart, Moscow, 1986).
23. A. Michels, J. V. Sengers, and P. S. van der Gulik, *Physica* **28**:1216 (1962).
24. H. M. Roder, NBSIR 84-3006 (National Bureau of Standards, Boulder, Colorado, 1984).
25. H. M. Roder and C. A. Nieto de Castro, *High Temp. High Press.* **17**:453 (1985).
26. H. M. Roder, *Int. J. Thermophys.* **6**:119 (1985).