

A Note on the Critical Enhancement of Transport Properties and Correlation Length of Fluids

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Abstract The thermal conductivity and viscosity of fluids are known to exhibit an enhancement due to critical fluctuations. Procedures proposed in the literature for estimating the correlation length determining the magnitude of these enhancements have been reviewed, and a recommendation to reduce complexity and computation time is presented.

Keywords Correlation length · Critical phenomena · Thermal conductivity · Transport properties

The thermal conductivity and viscosity of fluids are known to exhibit an enhancement, which is induced by the presence of long-range fluctuations in the vicinity of the critical point. In particular, the critical enhancement of the thermal conductivity is significant over a substantial range of densities and temperatures around the critical point. To account for this phenomenon, the thermal conductivity λ is decomposed as the sum of an enhancement, $\Delta_c \lambda$, caused by the presence of long-range critical fluctuations, and a background thermal conductivity, λ_b , which is the thermal conductivity to be

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expected in the absence of critical fluctuations [1]:

$$\lambda = \Delta_c \lambda + \lambda_b. \quad (1)$$

Asymptotically close to the critical point, $\Delta_c \lambda$ of a pure fluid diverges as [2,3]

$$\Delta_c \lambda \approx \frac{\rho C_P R_D k_B T}{6\pi \eta \xi}. \quad (2)$$

Here, ρ is the density, C_P is the isobaric specific heat capacity, T is the temperature, k_B is Boltzmann's constant, η is the shear viscosity, and ξ is a correlation length. The coefficient R_D is a universal dynamical amplitude ratio with a value close to unity [4,5].

To represent the thermal-conductivity enhancement of a pure fluid, including its non-asymptotic critical behavior, Eq. 2 is commonly extended to

$$\Delta_c \lambda = \frac{\rho C_P R_D k_B T}{6\pi \eta \xi} Y(\bar{q}_D \xi), \quad (3)$$

where \bar{q}_D is a fluid-specific Debye-like cutoff wave number for the critical fluctuations. In Eq. 3, $Y(\bar{q}_D \xi)$ is a crossover function such that $\lim_{y \rightarrow \infty} Y(y) = 1$ and $\lim_{y \rightarrow 0} Y(y) = 0$. Explicit expressions for the crossover function $Y(y)$ have been presented in the literature [6–8]. A review of the available options is presented elsewhere [9]. As an example, we consider here an approximate crossover function originally proposed by Olchowy and Sengers [6]

$$Y_{OS}(y) = \frac{2}{\pi} \left\{ \left[(1 - \kappa^{-1}) \arctan(y) + \kappa^{-1} y \right] - \left[1 - \exp \left(\frac{-1}{y^{-1} + y^2 \rho_c^2 / 3 \rho^2} \right) \right] \right\}, \quad (4)$$

where $\kappa = C_P / C_V$ is the heat-capacity ratio and ρ_c is the density at the critical point. This crossover function has been used to represent the critical thermal-conductivity enhancement for a large number of fluids, as reviewed in a recent publication [5].

In order to evaluate Eqs. 3 and 4, a procedure is needed for calculating the correlation length ξ . For this purpose, it is noted that at the critical density, $\rho = \rho_c$, the correlation length ξ and the susceptibility $\chi = \rho(\partial \rho / \partial P)_T$ asymptotically diverge near the critical temperature T_c as

$$\xi \approx \xi_0 |\Delta \bar{T}|^{-\nu} \text{ and } \chi \approx \Gamma_0 |\Delta \bar{T}|^{-\gamma}, \quad (5)$$

where $\Delta \bar{T} = (T - T_c) / T_c$ [10]. In these asymptotic power laws, $\nu \simeq 0.630$ and $\gamma \simeq 1.239$ are universal critical exponents [10]. Procedures for estimating the critical amplitudes, ξ_0 and Γ_0 , have been discussed elsewhere [5]. The asymptotic power-law behavior, given by Eq. 5, is then in practice generalized non-asymptotically [5] as

$$\xi = \xi_0(\Gamma_0^{-1}\chi)^{\nu/\gamma}. \quad (6)$$

A difficulty is that in Eqs. 3 and 4, the correlation length ξ is to be interpreted as that part of the correlation length associated with the critical fluctuations, which should vanish far away from the critical point as $\xi \rightarrow 0$. Hence, a modification of Eq. 6 is needed. The modification most frequently used is [6–8]

$$\Delta_c \xi \simeq \xi_0(\Gamma_0^{-1}\Delta\chi)^{\nu/\gamma}, \quad (7)$$

with

$$\Delta\chi = \chi(T, \rho) - \chi(T_R, \rho) \frac{T_R}{T}. \quad (8)$$

In Eq. 8, T_R is a reference temperature, where the critical enhancement is assumed to be negligibly small. Values adopted for T_R in the literature have varied from $1.5 T_c$ to $2 T_c$ [5]. In addition, the correlation length $\Delta_c \xi$ has to be set equal to zero when $\Delta\chi \leq 0$.

Use of Eq. 7 has some disadvantages, including that it cannot be readily extended to mixtures [11, 12]. It is not clear how to choose a reference temperature, since the correlation length of mixtures depends not only on temperature and density, but also on concentration. Therefore, some alternatives to Eq. 7 have been considered in the literature. A very simple representation adopted by Luettemer-Strathmann and Sengers is [11, 12]

$$\Delta_c \xi \simeq \xi_0 \left[(\Gamma_0^{-1}\chi)^{\nu/\gamma} - 1 \right]. \quad (9)$$

Kiselev and co-workers have adopted

$$\Delta_c \xi \simeq \xi_0(\Gamma_0^{-1}\chi)^{\nu/\gamma} \left[1 - \left(\frac{r_0}{\xi_0(\Gamma_0^{-1}\chi)^{\nu/\gamma}} \right)^2 \right] \quad (10)$$

with $r_0 = \xi_0$ or $r_0 = \bar{q}_D^{-1}$ [13], and subsequently [14–17]

$$\Delta_c \xi \simeq \xi_0(\Gamma_0^{-1}\chi)^{\nu/\gamma} \exp \left[\frac{-1}{\bar{q}_D \xi_0(\Gamma_0^{-1}\chi)^{\nu/\gamma}} \right]. \quad (11)$$

Just like Eq. 7, $\Delta_c \xi$ should be set equal to zero when the right-hand sides of Eqs. 9 and 10 become negative. In practice, Eqs. 9–11 have been used in the Ornstein–Zernike approximation, $\gamma = 2\nu$ [11–17]. Since a reliable estimate for the correlation length for the critical enhancement of the transport properties is most important close to the critical point, we see no pressing need for adopting the approximation, $\gamma = 2\nu$.

We have compared the various alternatives by using them to calculate the critical thermal-conductivity enhancement of H_2O , for which a good representation of the

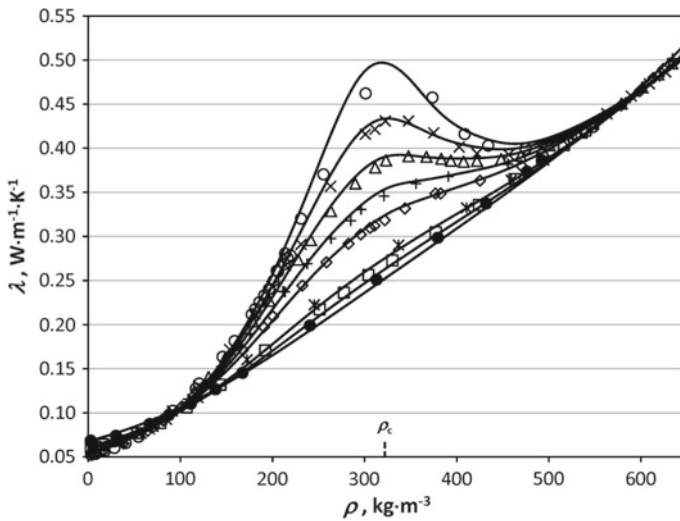


Fig. 1 Thermal conductivity of H₂O in the critical region. Symbols indicate experimental thermal-conductivity data reported by Tufeu and Le Neindre [19]. Curves represent theoretical values calculated with the aid of Eq. 7 for the correlation length [18]. Isotherms are designated by the symbols: ○, 652 K; ×, 655 K; △, 659 K; +, 665 K; ◇, 673 K; *, 706 K; □, 729 K; ●, 784 K

critical thermal-conductivity enhancement in terms of Eq. 7 is available [18]. Our conclusion is that we recommend replacing Eq. 7 by

$$\Delta_c \xi = \xi_0 (\Gamma_0^{-1} \chi)^{\nu/\gamma} \exp\left(\frac{-1}{\Gamma_0^{-1} \chi}\right), \quad (12)$$

which is essentially an exponential form of Eq. 10 with the Ornstein–Zernike approximation and $r_0 = \xi_0$ in the argument of the exponential term. Hence, the argument of the crossover function $Y(y)$ in Eq. 3 is to be evaluated as $y = \bar{q}_D \Delta_c \xi(\rho, T)$.

In Figs. 1 and 2, we show comparisons between the experimental thermal-conductivity data of Tufeu and Le Neindre [19] and the values calculated from Eqs. 1, 3, and 4, with $R_D = 1.01$ and values for the critical amplitudes and the background thermal conductivity as determined by Huber et al. [18] for H₂O. Figure 1 shows the theoretical values when use is made of Eq. 7 for the correlation length $\Delta_c \xi$ with $T_R = 1.5T_c$ in Eq. 8. Figure 2 shows the theoretical values when use is made of Eq. 12 for the correlation length $\Delta_c \xi$. The corresponding deviations between the experimental data and the alternative expressions, Eqs. 7 and 12, for the correlation length are shown in Fig. 3a, b, respectively. The deviations resulting from the two procedures are virtually indistinguishable. Deviations farther away from the critical point may be up to 2%, which is within the accuracy the theory can predict the difference between a critical-enhancement and a background thermal conductivity. The differences resulting from the two procedures remain even smaller when one adopts $T_R = 2T_c$ in Eq. 8, as originally recommended by Olchowy and Sengers [6], and which has been used by a number of investigators, as reviewed in [5]. The viscosity also exhibits a critical

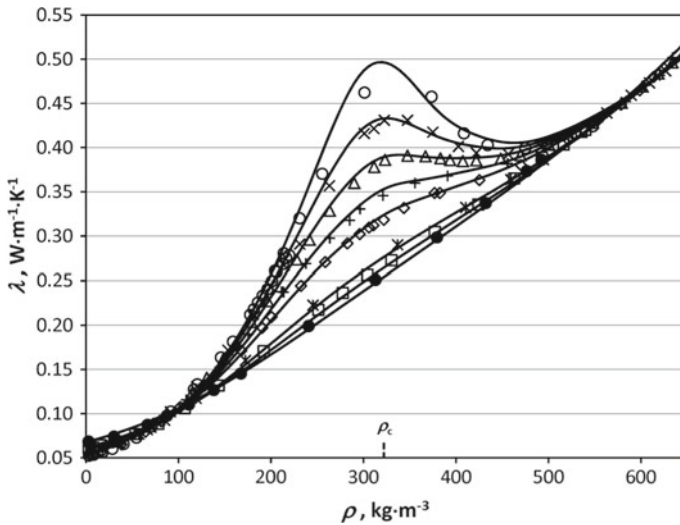


Fig. 2 Thermal conductivity of H₂O in the critical region. Symbols indicate experimental thermal-conductivity data reported by Tufeu and Le Neindre [19]. Curves represent theoretical values calculated with the aid of Eq. 12 for the correlation length. Isotherms are designated by the symbols: ○, 652 K; ×, 655 K; △, 659 K; +, 665 K; ◇, 673 K; *, 706 K; □, 729 K; ●, 784 K

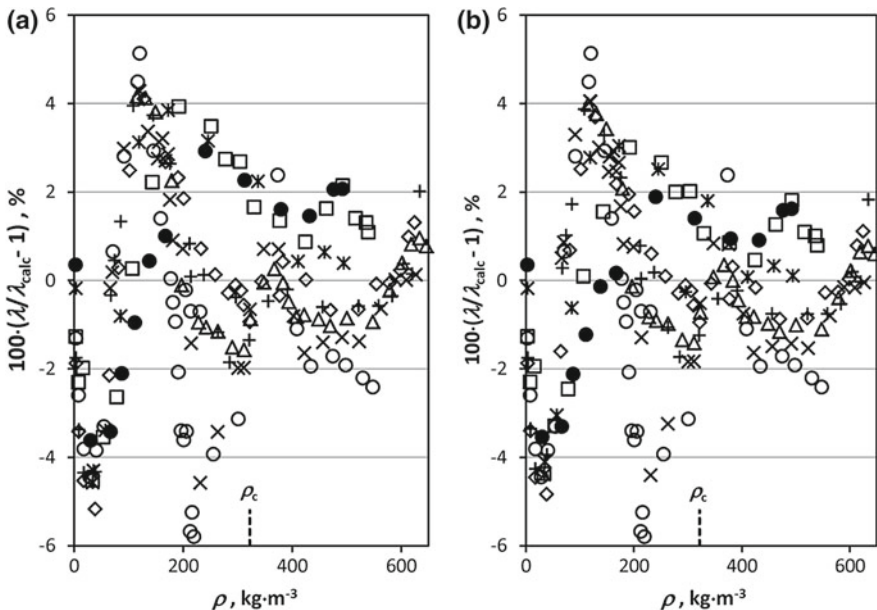


Fig. 3 Deviations between experimental thermal conductivity data reported by Tufeu and Le Neindre [19] and theoretical values calculated with (a) Eq. 7 and (b) Eq. 12. Isotherms are designated by the symbols: ○, 652 K; ×, 655 K; △, 659 K; +, 665 K; ◇, 673 K; *, 706 K; □, 729 K; ●, 784 K

enhancement, although much weaker than that of the thermal conductivity [20]. Use of the two procedures for calculating the correlation length yields the same description for the viscosity near the critical point as well.

Use of Eq. 12 for calculating the correlation length in the expressions for the critical enhancements of the transport properties has a number of advantages, even in the case of one-component fluids. First, Eq. 12 does not require any conditional definitions anywhere, such as $\Delta\chi = 0$ when $\Delta\chi \leq 0$ in Eq. 7. As a consequence, the correlation length calculated from Eq. 12 will be a smooth function of density and temperature everywhere. Second, one no longer needs to evaluate the susceptibility at two temperatures for every data point, namely, at the actual temperature and at a reference temperature T_R . Most importantly, a complication arises in calculating the thermal conductivity in the critical region when the requirement of Eq. 8, namely, that the compressibility also be calculated at the density of interest ρ at T_R cannot be met. Many molecules are not chemically stable at 1.5 times their critical temperature. Even when the equation of state is valid at T_R , it may not extend to the higher pressures corresponding to ρ at T_R . As an example, this problem is encountered in the formulation for the thermal conductivity of H₂O for industrial use adopted by the International Association for the Properties of Water and Steam [21]. The validity of the IAPWS Industrial Formulation 1997 for the thermodynamic properties of H₂O [22] does not extend to the high pressures required at the reference temperature $T_R = 1.5 T_c$. As a consequence, an additional auxiliary program was needed to represent the susceptibility at the reference temperature [18, 21] in this industrial formulation. Use of Eq. 12 will avoid this complication and simplify programming. It is expected that the alternative procedure may reduce the computation time for calculating the critical enhancement of the thermal conductivity of fluids.

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