Thermal Conductivity Enhancement of Pure Fluids Along the Critical Isochore

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The critical point is a point of incipient instability. As a consequence large density fluctuations are present in fluid in the vicinity of the gas-liquid critical point. These density fluctuations cause an anomalous behavior of many thermophysical properties in the critical region. For instance, the isothermal compressibility, the thermal expansion coefficient, and the specific heat of fluids diverge near the critical point. Anomalous effects are also encountered when one studies the behavior of the thermal conductivity and the viscosity of fluids near the critical point. While a critical enhancement in the thermal conductivity of fluids has been noticed up to temperatures 20% above the critical temperature, the critical enhancement in the viscosity of fluids only appears at temperatures less than 3% from the critical temperature. Thus, one must not ignore certain critical anomalies as a system's operating conditions approach a critical point.

Theories and experimental data that exist at the present time do not allow unambiguous resolution of the question of the character of the thermal conductivity near the critical point of a pure fluid. Even the modern theories include a number of adjustable parameters or they possess physical properties at the critical point that are very difficult or impossible at present to measure or to predict. This lack of information makes current theories meaningless for the estimation of transport properties in the critical region. Also, no unified approach has been attempted to predict, in a generalized manner, the critical thermal conductivity behavior. In this connection, a generalized approach has been made to find the parameters that strongly influence the thermal conductivity enhancement of pure fluids along the critical isochore.

Parameter Estimation

In order to represent the behavior of the thermal conductivity of fluids in the critical region, it is customary to separate the total thermal conductivity k into the sum of an ideal k_{id} that would exist in the absence of the anomalous critical effect, and a critical enhancement contribution Δk:

$$k(T,\rho) = k_{id}(T,\rho) + \Delta k(T,\rho) \tag{1}$$

The thermal conductivity enhancement of pure fluids along the critical isochore is described by a simple power law proposed by Sengers (1972),

$$\Delta k_c = \Delta k(\epsilon, \rho_c) = \Lambda \epsilon^{-\psi} \tag{2}$$

where Λ is the critical amplitude specific to each fluid, ψ is the critical exponent having a universal constant for all fluids irrespective of molecular details, and ϵ is the reduced temperature defined as $(T - T_c)/T_c$.

A dimensional analysis approach for the dependence of Δk upon temperature and density using the critical point as a frame of reference, suggests the relationship expressed as:

$$\Delta k_c \beta / \alpha(Z_c) = \epsilon^{-\psi} \tag{3}$$

where $\beta = M^{1/2}T_c/P_c^{3/2}v_c^{5/6}$ is the thermal conductivity parameter and α is the characteristic constant specific to each fluid. Experimental measurements available in the literature for the anomalous enhancement of thermal conductivity in the critical region of 11 fluids including nonpolar, polar, quantum, and even associating substances have been utilized for the development of a generalized method capable of predicting this transport property in this region, and particularly along the critical isochore. Figure 1 indicates that Δk_c has a linear dependence on ϵ in log-log coordinates with a slope of approximately 0.63 for $\epsilon < 0.01$, which coincides with the critical exponent of correlation length predicted from two modern theories, namely renormalization group (Siggia et al., 1976) and mode coupling (Kawasaki, 1971). A linear regression method was used to obtain the best α values for 11 fluids. These values are presented in Table 1 with other physical constants; they range from $\alpha = 0.01011$ for helium-3 ($Z_c = 0.309$) to $\alpha = 0.08294$ for water ($Z_c = 0.228$).

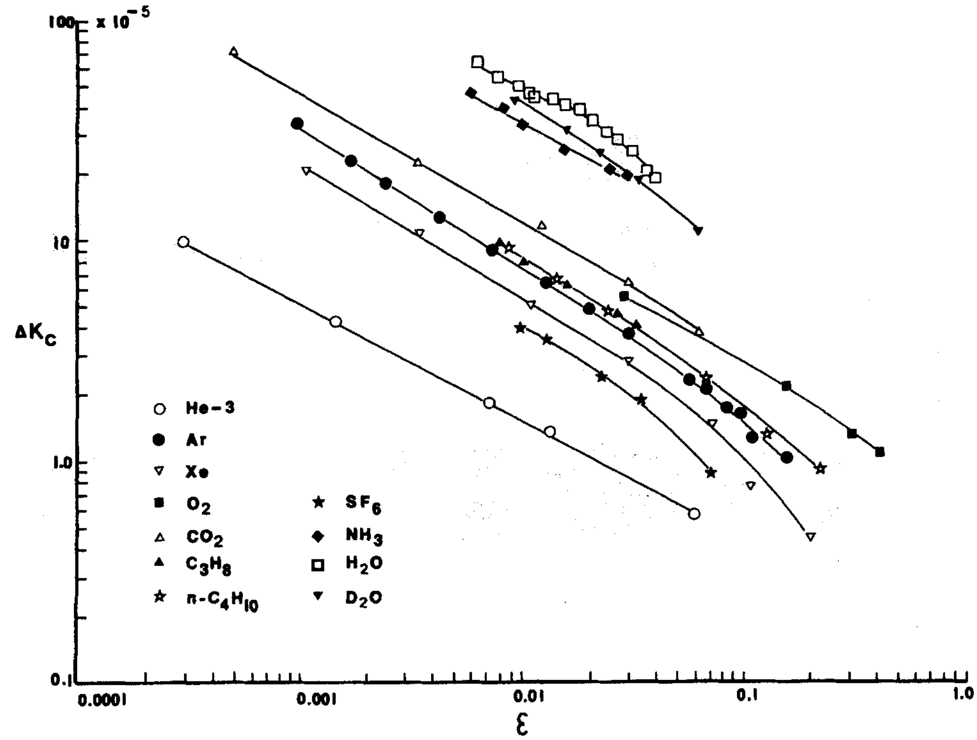

Figure 1. Relationship between Δk_c and ϵ.

This fact indicates that both the critical compressibility factor and the thermal conductivity parameter are the key parameters strongly influencing the enhancement of the thermal conductivity in the vicinity of the critical point.

The relationship between the α value and the corresponding critical compressibility facter is shown in Figure 2 and expressed as

$$\alpha(Z_c) = -0.348 + 3.938 Z_c - 8.996 Z_c^2 \tag{4}$$

Figure 3 shows the generalized relationship between the normalized thermal conductivity, $\Delta k_c \beta/\alpha$, and the normalized temperature for 11 fluids. It can be seen in this log-log plot that the linear dependence of $\Delta k_c \beta/\alpha$ upon ϵ with a slope of 0.63 is well applied for a temperature range of $\epsilon < 0.1$, while the nonlinear relationship between $\Delta k_c \beta/\alpha$ and ϵ is shown for $\epsilon > 0.1$, which means that the critical enhancement of thermal conductivity decays with a critical exponent more negative than -0.63 and further that the critical exponent is a function of ϵ. This predictive approach only requires the critical constants of a pure fluid for the prediction of the thermal conductivity enhancement along the critical isochore. However, the validity of this method remains to be tested further when additional experimental information regarding thermal conductivity enhancement in the critical region becomes available.

Conclusion

A generalized approach has been made for the prediction of the thermal conductivity enhancement along the critical iso-

Table 1. Basic Constants of Fluids Used in Study

Substances	M	T_c K	P_c atm	V_c cm^3/g · mol	Z_c	β	α	Reference
Helium-3	3.016	3.31	1.15	73.0	0.309	0.13048	0.01011	Pittman et al. (1982)
Argon	39.948	150.76	48.13	75.0	0.292	0.07818	0.03271	Trappeniers (1981)
Xenon	131.300	289.73	57.64	118.3	0.287	0.14210	0.04373	Trappeniers (1981)
Oxygen	32.000	154.58	49.77	73.4	0.288	0.06946	0.04134	Roder (1982)
Carbon dioxide	44.010	304.19	72.85	94.4	0.276	0.07339	0.04503	Michels et al. (1962)
Propane	44.097	369.80	41.90	203.0	0.281	0.10813	0.05123	Le Neindre et al. (1984)
n-Butane	58.124	425.20	37.50	255.0	0.274	0.13940	0.06491	Le Neindre et al. (1984)
Sulfur-hexafluoride	146.050	318.70	37.10	198.0	0.281	0.20782	0.04520	Letaief et al. (1986)
Ammonia	17.031	405.40	112.00	72.5	0.244	0.03977	0.07668	Tufeu et al. (1981)
Water	18.015	647.07	217.59	55.5	0.228	0.03010	0.08294	Sirota et al. (1976)
Heavy water	20.031	644.00	213.80	55.6	0.225	0.03240	0.07632	Tufeu et al. (1986)

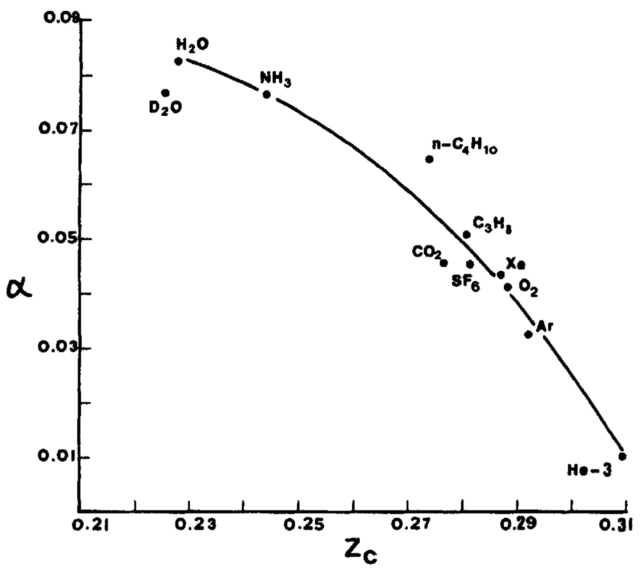

Figure 2. Dependence of α upon Z_c.
—Eq. 4.

chore. Both the critical compressibility factor and the thermal conductivity parameter were found to be the key parameters for understanding the anomalous behavior of thermal conductivity in the critical region.

Acknowledgment

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Notation

k – thermal conductivity, cal/cm · s · K
M – molecular weight
P – pressure, atm
T – temperature
V – molar volume, $cm^3/g \cdot mol$
Z_c – critical compressibility factor

Greek letters

α – constant, Eq. 4
β – thermal conductivity parameter, $M^{1/2}T_c/P_c^{3/2}v_c^{5/6}$
ϵ – reduced temperature, $(T - T_c)/T_c$
ρ – density, g/cm^3
ψ – critical exponent, Eq. 2
Λ – critical amplitude, Eq. 2

Subscript

c – critical constant

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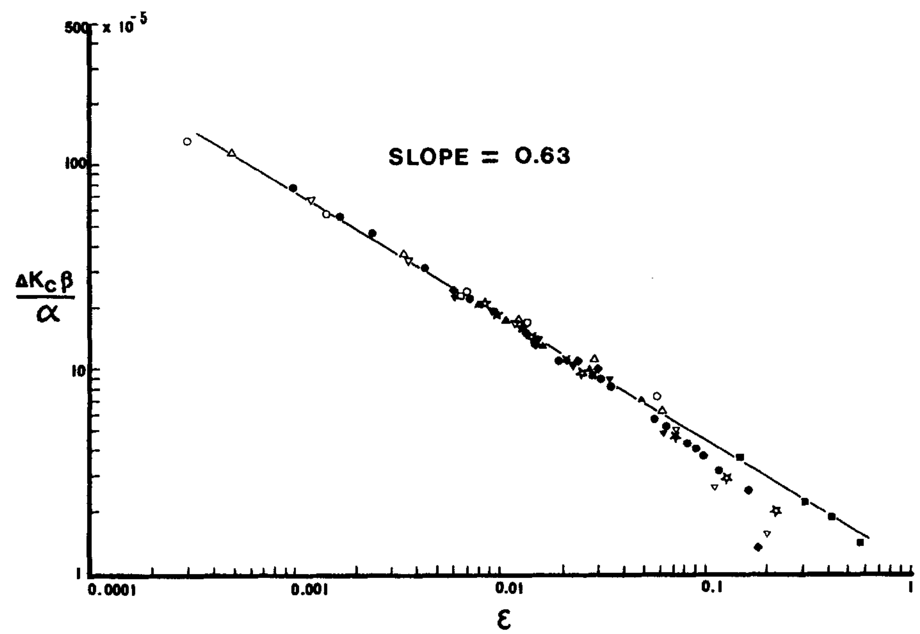

Figure 3. Generalized relationship between $\Delta k_c\beta/\alpha$ and ϵ.
Symbols as in Figure 1

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