# THERMAL CONDUCTIVITY OF PURE FLUIDS IN THE CRITICAL REGION.

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**Abstract**—A generalized approach has been made to find the parameters strongly influencing the anomalous thermal conductivity behavior in the critical point region. For an analysis of the mathematical character of the critical anomaly, the two commonly used thermodynamic variables, temperature and density, and the two characteristic parameters, critical compressibility factor, Zc, and De Boer quantum parameter, $\Lambda^*$, have been adopted.

## INTRODUCTION

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 speicific heat of fluids all diverge at the gas-liquid 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.

The thermal conductivity of fluids near the critical point is commonly separated into a normal thermal conductivity, $\Delta k_{normal}$, in the absence of critical fluctuations and a critical enhancement, $\Delta k$, due to the critical fluctuations:

$$k = k_{normal} + \Delta k \qquad (1)$$

The thermal conductivity as a function of density is schematically shown in Fig. 1. Outside the critical region, the thermal conductivity, k, is to be identified with the normal thermal conductivity, $k_{normal}$. Inside the critical region, $k_{normal}$ is defined empirically by extrapolating the behavior of the normal thermal conductivity outside the critical region into the critical region. Excess thermal conductivity is defined as,

$$k_{excess} = k_{normal} - k^* \qquad (2)$$

Where k* is the thermal conductivity at the same temperature of fluids in the dilute gaseous state.

## THEORETICAL BACKGROUND

### 2.1. Brokaw's Theory

Attempts to treat quantitatively the enhancement of thermal conductivity in the critical region have been limited because of the abrupt behavior in this region. To explain this anomalous behavior, the enhancement was attributed to the association and dissociation of cluster diffusing in the presence of temperature gradient. This approach was pursued to a considerable degree by Brokaw [1].

He assumed that the thermal conductivity near the critical point could be described in terms of reacting gas. While he recognized that there exists a spectrum of clusters sizes, for simplicity, the gas was assumed to consist of a monomer and a single large cluster of n-monomers, i.e.,

$$nX_1 - X_n \qquad (3)$$

To obtain the anomalous part of thermal conductivity in the critical region, he developed an expression as,

$$\Delta k = C_1 \; C_{pr} D_1 (D_{1n}/D_1) \qquad (4)$$

where the reacting specific heat, $C_{pr}$, is defined as an excess specfic heat,

$$C_{pr} = C_p(P, T) - C_{po}(T) \qquad (5)$$

and $C_1$ is a adjustable constant. This constant is determined by matching the theory to a single experimental data point. Once $C_1$ is determined, the thermal conductivity over the entire region can be found. However, this

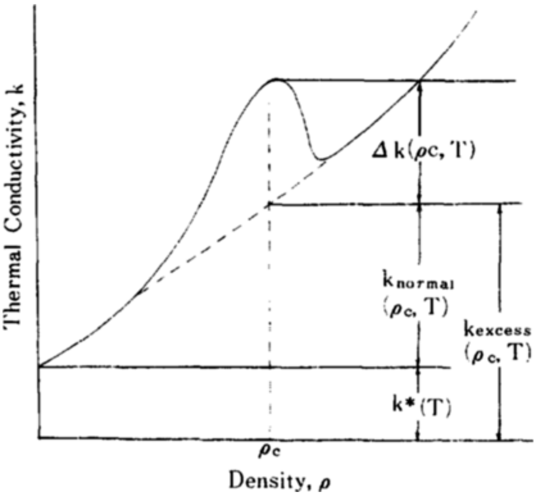

**Fig. 1. Schematic representation of the thermal conductivity as a function of density at a temperature slightly above the critical temperature.**

approach is difficult to use because it requires the introduction of many empirically determined constants.

## 2.2 Mode Coupling Theory

Theoretical prediction of the mode coupling theory can be obtained from the simple argument of Arcovito et al. [2] which assumed that the mobility of clusters is purely a diffusional process. For the diffusional involvement of these clusters, the Einstein relation for the diffusion coefficient can be expressed as follows:

$$D = kT/\zeta \tag{6}$$

where k is the Boltzmann constant, T is temperature and $\zeta$ is a friction coefficient. When this friction coefficient is identified with the hydrodynamic friction coefficient predicted by Stoke's law for a spherical droplet of radius $\xi$, it becomes,

$$\zeta = 6\pi\mu\xi \tag{7}$$

where $\mu$ is the shear viscosity. Substituting Equation (7) into Equation (6), the diffusion coefficient becomes,

$$D = kT/6\pi\mu\xi \tag{8}$$

Kawasaki [3] assumed a direct analogy between this diffusion coefficient and thermal diffusivity to couple these two phenomena into the relationship

$$\Delta k/\rho\Delta C_p = kT/6\pi\mu\xi \tag{9}$$

where $\Delta k$ represents the thermal conductivity enhancement in the critical point region and $\Delta C_p = C_p - C_v$. In the derivation of Equation (9) it is assumed that the shear viscosity of $\mu$ does not exhibit any anomalous behavior near the critical point. This assumption is not strictly justified, but the anomalous behavior of $\mu$ turns out to be sufficiently small so that it can be neglected for most practical purposes.

Equation (9) can be rearranged to present the enhancement of thermal conductivity as follows:

$$\Delta k = (kT/6\pi\mu\xi)\rho(C_p - C_v) \tag{10}$$

In order to make Equation (10) vanish for conditions removed from the critical region, Hanley et al. [4] extended Equation (10) using an empirical asymptotic function as follows:

$$\Delta k = (kT/6\pi\mu\xi)\rho(C_p - C_v)f(\Delta T^*, \Delta\rho^*) \tag{11}$$

where the function $f(\Delta T^*, \Delta\rho^*)$ satisfies the boundary conditions,

$$\lim_{\Delta T^*, \Delta\rho^* \to 0} f(\Delta T^*, \Delta\rho^*) = 1$$

and

$$\lim_{\Delta T^*, \Delta\rho^* \to \infty} f(\Delta T^*, \Delta\rho^*) = 1 \tag{12}$$

where $\Delta T^* = T_R - 1$ and $\Delta\rho^* = \rho_R - 1$. Utilizing the measurements for the thermal conductivity enhancement of carbon dioxide, Hanley et al. proposed the form and developed the coefficients of this function to be,

$$f(\Delta T^*, \Delta\rho^*) = \exp(-18.66\,|\Delta T^*|^2) \cdot \exp(-4.25\,|\Delta\rho^*|^4) \tag{13}$$

Using the thermodynamic relation,

$$C_P - C_V = (T/\rho^2)\,(\partial P/\partial T)^2_\rho(\partial\rho/\partial P)_T \tag{14}$$

where $(1/\rho)\,\partial\rho/\partial P)_T$ is the isothermal compressibility and substituting Equation (14) into Equation (11) the following relationship results:

$$\Delta k = [(kT^2/6\pi\mu\xi)\cdot(\partial P/\partial T)_\rho\,(\partial\rho/\partial P)_T]/\exp(18.66\,|\Delta T^*|^2 + 4.25\,|\Delta\rho^*|^4) \tag{15}$$

where $\xi$ is a long range correlation length that represents the average radius of the critical state clusters. This long range correlation length can be determined experimentally from light scattering or X-ray scattering data. Assuming that the correlation length, $\xi$, can be approximated by the Ornstein and Zernike formula, Sengers [5] obtained the following relationship,

$$\xi = R(nkTK_T)^{1/2} \tag{16}$$

where n is the number density, k Boltzmann's constant, R a proportionality constant, usually referred to as short range correlation length and $K_T$ isothermal compressibility.

The expression given by Equation (11) possesses semi-empirical arguments for its development and satisfactorily represents the thermal conductivity enhancement in the critical region for a few substances for which experimental information is available. Additional thermal conductivity measurements in this region are needed to test its applicability beyond the substances considered. However, it should be recognized that the application of this relationship requires extensive information for a substance in the critical region. More often than not, such information is not readily accessible and therefore the application of Equation (11) becomes limited to substances whose physical properties are well defined in the critical region.

## GENERALIZED TREATMENT OF THERMAL CONDUCTIVITY BEHAVIOR IN THE CRITICAL POINT REGION

The throries 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 which are very difficult or impossible in the present level to measure or predict. This lack of information makes current theories meaningless for the estimation of transport properties in the ciritical region. Also, no unified approach in the generalized manner has been attempted for critical thermal conductivity behavior.

In this connection, a qualitative approach has been made to find the parameters strongly influencing the thermal conductivity in the critical region. As a first approximation, the two commonly used thermodynamic variables, temperature and density, and the two characteristic parameters, critical compressibility factor, $Z_c$, and De Boer quantum parameter, $\Lambda^*$, have been adopted. Therefore, the critical thermal conductivity enhancement, $\Delta k$, can be generally
expressed as,

$$F(\Delta k, \Delta T^*, \Delta\rho^*; Z_c, \Lambda^*) = 0 \qquad (17)$$

where $\Lambda^*$ is defined as,

$$\Lambda^* = h/\sigma(m\varepsilon)^{1/2} \qquad (18)$$

where h is Planck's constant, m the mass of a molecule, $\varepsilon$ the maximum energy of attraction and $\delta$ the collision diameter for Lennard-Jones potential. The quantity $\Lambda^*$ assumes large values for the quantum gases due to the small values of the three factors $\delta$, m and $\varepsilon$ of these gases.

According to the scaling method, Equation (17) may be expressed with the scaling functions $f(\Delta\rho^*)$ and $g(\Delta\rho^*)$ for the remaining variables $\Delta k$ and $\Delta T^*$ and written as,

$$X[\Delta k/f(\Delta\rho^*), \Delta T^*/g(\Delta\rho^*); Z_c, \Lambda^*] = 0 \qquad (19)$$

which can be solved for $\Delta k/f(\Delta\rho^*)$ as,

$$\Delta k = f(\Delta\rho^*)\, U[\Delta T^*/g(\Delta\rho^*); Z_c, \Lambda^*] \qquad (20)$$

In Equation (20) $\Delta\rho^*$ was chosen as a scaling variable for the remaining variables, $\Delta k$ and $\Delta T^*$. $\Delta T^*$ can be also selected as a scaling variable to yield the following expression:

$$\Delta k = h(\Delta T^*)\, V[\Delta\rho^*/k(\Delta T^*); Z_c, \Lambda^*] \qquad (21)$$

The power law assumption near the critical point indicates that the scaling functions $f(\Delta\rho^*)$, $g(\Delta\rho^*)$, $h(\Delta T^*)$ and $k(\Delta T^*)$ can be expressed as,

$$\begin{aligned} f(\Delta\rho^*) &= c\,|\Delta\rho^*|^{\lambda} \\ g(\Delta\rho^*) &= c'\,|\Delta\rho^*|^{\mu} \\ h(\Delta T^*) &= d\,|\Delta T^*|^{\phi} \\ k(\Delta T^*) &= d'\,|\Delta T^*|^{\pi} \end{aligned} \qquad (22)$$

However, the conditions under which both Equation (20) for $\Delta\rho^*$- scaling and Equation )21) for $\Delta T^*$-scaling describe the same physical function must be established. The substitutuon of the power law assumptions, Equation (22) into Equation (20) yields the following expression:

$$\begin{aligned} \Delta k &= c\,|\Delta\rho^*|^{\lambda} U[\Delta T^*/c'\,|\Delta\rho^*|^{\mu}; Z_c, \Lambda^*] \\ &= c(\Delta T^*)^{\lambda/\mu}(|\Delta T^{*1/\mu})^{\lambda} U \\ &\quad [(|\Delta\rho^*|/\Delta T^{*1/\mu})^{-\mu}/c'; Z_c, \Lambda^*) \\ &= c(\Delta T^*)^{\lambda/\mu} V[|\Delta\rho^*|/\Delta T^{*1/\mu}; Z_c, \Lambda^*] \end{aligned} \qquad (23)$$

where the functional relationship between U and V for any physical variable, V, can be written as

$$V(v; Z_c, \Lambda^*) = v^{\lambda} U(v^{-\mu}/c'; Z_c, \Lambda^*) \qquad (24)$$

The comparision of Equation (21) with Equation (23) produces the relationships, which can be expressed as,

$$h(\Delta T^*) = c(\Delta T^*)^{\lambda/\mu} \text{ and } k(\Delta T^*) = \Delta T^{*1/\mu} \qquad (25)$$

Therefore, the relationships of the exponents in Equation (25) can be represented as follows:

$$\phi = \lambda/\mu \qquad \text{and} \qquad \pi = 1/\mu \qquad (26)$$

Thus, Equation (20) and Equation (21) are equivalent if the scaling functions $f(\Delta\rho^*)$, $g(\Delta\rho^*)$, $h(\Delta T^*)$ and $k(\Delta T^*)$ are pure powers. However, Equation (20) will be used as a basis for further development of the generalization of thermal conductivity behavior near the critical point. The values of the constant c' and the exponent $\mu$ in Equation (20) may be obtained from the critical exponent along the coexitence curve, $\beta$, and the variable x which were expressed as

$$\Delta\rho^* = \pm B\,|\Delta T^*|^{\beta} \qquad (27)$$

and $$x = \Delta T^*/|\Delta\rho^*|^{1/\beta} \qquad (28)$$

Since $x = x_0$ along the coexistence curve, the following relationships may be justified;

$$c' = x_0 = B^{1/\beta} \qquad \mu = 1/\beta \qquad (29)$$

Thus, the thermal conductivity behavior near the critical point in a comprehensive manner can be expressed as,

$$\Delta k\,\psi_c/f(Z_c, \Lambda^*) = |\Delta\rho^*|^{\lambda} W(x/x_0) \qquad (30)$$

where the thermal conductivity parameter, $\psi_c = M^{1/2}T_c/P_c/^{3/2}v_c^{5/6}$, was obtained from dimensional analysis. In Equation (28), the absolute value $\Delta\rho^*$ is taken if $\Delta k\psi_c$ is symmetric with respect to $\rho = \rho_c$. Table 1

**Table 1.** Basic parameters and deviations resulting from Eq. (32).

| Gas / Property | He-3 | Ar | Xe | $CO_2$ | $H_2O$ |
|---|---|---|---|---|---|
| M | 3.016 | 39.948 | 131.30 | 44.01 | 18.015 |
| $T_C$, °K | 3.3082 | 150.76 | 289.73 | 304.11 | 647.13 |
| $P_C$, atm | 1.13 | 48.1 | 57.64 | 72.79 | 217.6 |
| $\rho_C$, $g/cm^3$ | 0.0045 | 0.533 | 1.110 | 0.468 | 0.322 |
| $v_C$, $\frac{cm^3}{g\text{-mole}}$ | 72.99 | 74.95 | 118.29 | 94.04 | 56.31 |
| $z_C$ | 0.305 | 0.291 | 0.287 | 0.274 | 0.231 |
| $\psi$ | 0.1340 | 0.0783 | 0.1421 | 0.0737 | 0.0298 |
| $\sigma$, A | 2.56 | 3.542 | 4.047 | 3.941 | 2.641 |
| $\varepsilon/\kappa$, °K | 10.2 | 93.3 | 231.0 | 195.2 | 809.1 |
| $\Lambda^*$ | 3.082 | 0.202 | 0.0621 | 0.120 | 0.137 |
| $x_o$ | 0.489 | 0.183 | 0.183 | 0.141 | 0.100 |
| f | 0.0029 | 0.0532 | 0.0465 | 0.0569 | 0.1557 |
| No. of points | 4 | 6 | 72 | 60 | 26 |
| % Dev. | 8.24 | 12.87 | 6.81 | 6.38 | 6.50 |

lists the values of $\psi_c$, $Z_c$, $\Lambda^*$ and $x_o$ for pure fluids investigated in this study. The values of $x_o$ were taken from Sengers et al.[6]. The thermal conductivity data of helium-3 [7], argon [8], xenon [9], carbon dioxide [10] and water [11] available in the literature were used to show the characteristic behavior of each fluid. Fig. 2. indicates that the anomalous parts of the dimensionless thermal conductivities along the critical isochore, $\Delta k_c(\rho_c, \Delta T^*)\psi_c$, for these fluids have a linear dependence on $\Delta T^*$ in log-log coordinates with a slope of approximately 0.63, but with a slight curvature removed from the critical temperature. Therefore,

$$\Delta k_C\psi_C/f(Z_C, \Lambda^*) \propto |\Delta T^*|^{-\psi} \tag{31}$$

In this figure, helium-3 with $Z_c$ = 0.305 and $\Lambda^*$ = 3.082 has the lowest value of $\Delta k_C\psi_C$ and water with $Z_c = 0.231$ and $\Lambda^*$ = 0.137, the highest. This fact infers that the critical compressibility factor and De Boer quantum parameter strongly influence the enhancement of the thermal conductivity near the critical point. However, additional experimental works with different types of fluids are needed to establish the actual functional relationship between $\Delta k_C\psi_C$ and $Z_c$ and $\Lambda^*$.

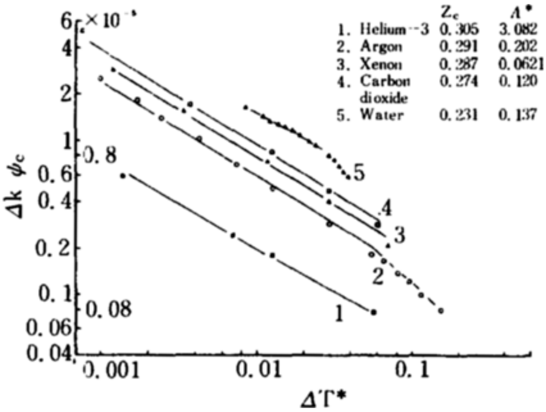

**Fig. 2. Relationship between the thermal conductivity along the critical isochore, $\Delta k\psi_C$, and the normalized temperature, $\Delta T^*$.**

It should be noted that Equation (30) has been developed under the assumptions that the thermal conductivity enhancement, $\Delta k$, is symmetric along the critical isochore, i.e., $\rho = \rho_c$, and follows a power-law behavior. The existence of a small asymmetry in $\Delta k$ has been confirmed in many experimental studies. Thus, it becomes necessary to introduce a symmetrizing factor in Equation (30) to overcome the asymmetric behavior of $\Delta k$ with respect to $\rho = \rho_c$. The symmetrizing function $f(\rho, T)$ can be defined by the condition:

$$\begin{aligned} & f(\rho_C - \Delta\rho, T)\Delta k(\rho_C - \Delta\rho, T) \\ & = f(\rho_C + \Delta\rho, T)\Delta k(\rho_C + \Delta\rho, T) \end{aligned} \tag{32}$$

The symmetrizing function $f(\rho, T)$, was empirically found to be $\rho_R^{0.5}$. In Equation (30) $\Delta k$ has to be changed to the symmetrized function, $\Delta k\rho_R^{1/2}$ so that the power law assumptions can be justified in the neighborhood of the critical point.

$$\Delta k\psi_C\rho_R^{1/2}/f(Z_C, \Lambda^*) = |\Delta\rho^*|^{\lambda} W(x/x_o) \tag{33}$$

The value of $\lambda$ is assumed to be temperature dependent in order to more or less overcome the limitation of the power-law assumption. The generalized behavior of the thermal conductivity enhancement has been assumed to have the functional expression of

$$\begin{aligned} \log[\Delta k\psi_C\rho_R^{0.5}|\Delta\rho^*|^{cT_R^r} f(Z_C, \Lambda^*)] = a[\log((x+x_o)/ \\ x_o)]^p + b[\log((x+x_o)/x_o)]^q \end{aligned} \tag{34}$$

where a, b, c, p, q and r are assumed to be constants applicable to all substances. A nonlinear regression analysis with the experimental measurements of xenon by Oosting have been used to produce the values of

a = −0.770858
b = −0.482894
c = 2.260902

p = −0.457740
q = 0.177897
r = 0.006463

Equation (34) with these constants has been applied to heliurn-3, argon, carbon dioxide and water to yield the values of $f(Z_c, \Lambda^*)$ for these substances which are presented in Table 1. The generalized relationship for the thermal conductivity enhancement of these five substances are shown in Fig. 3. The average deviations between the calculated values using Equation (34) and the experimental values are included in Table 1.

It is difficult at this time to find the relationship between f and $Z_c$ and $\Lambda^*$ with this limited information. Furthermore, the power law assumption can only be applied in the close vicinity of the critical point. Therefore,

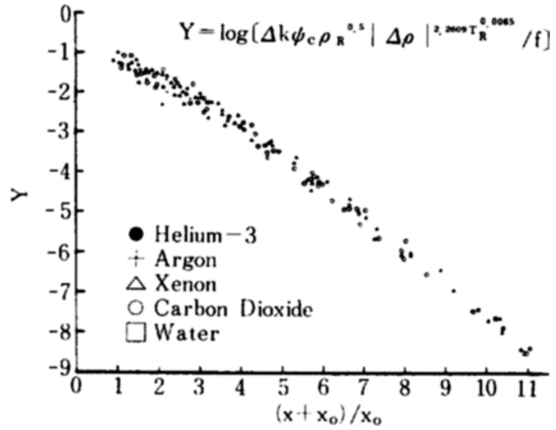

**Fig. 3. Generalized behavior of the thermal conductivity enhancement of fluids in the vicinity of the critical point.**

this assumption has to be changed when an accurate equation of state along the coexistence curve is established.

## CONCLUSION

A generalized equation has been formulated for the critical enhancement to the thermal conductivity which represents existing experimental data in the critical region. This equation is based on the thermodynamic behavior in the vicinity of the gas-liquid critical point with well established thermodynamic properties. In spite of the increasing demand on accurate data for thermal conductivity near the critical point, a few experiments for simple fluids have been carried out. Thus, future works, both experimental and analytical, are needed to resolve the issues associated with the abnormal behavior of the thermal conductivity in the critical point region in order to this generalized relationship to many different types of substances.

## NOMENCLATURE

a, b, c : constants
D : self-diffusivity, $Cm^2$/sec
h : Planck's constant
k : thermal conductivity, cal/sec. cm °K
$\Delta k$ : critical thermal conductivity enhancement, cal/sec. cm °K
m : mass of a molecule
p, q, r : constants
$\Delta T^*$ : normalized temperature, $T_R$-1
x : density-temperature scaling variable
$x_0$ : value of scaling variable, x, along the coexistence curve
$Z_c$ : critical compressibility factor

**Greek letters**

$\beta$ : critical exponent for coexistence curve
$\varepsilon$ : Lennard-Jones force constant, maximum energy of attraction
$\zeta$ : friction coefficient
$\kappa$ : Boltzmann constant
$\Lambda^*$ : De Boer quantum parameter
$\lambda$, $\mu$ : exponents in equation (20)
$\mu$ : viscosity, poises
$\xi$ : long range correlation length
$\pi$, $\phi$ : exponents in equation (20)
$\Delta\rho^*$ : normalized density, $\rho_R - 1$
$\sigma$ : average distance between molecular centers
$\psi_c$ : thermal conductivity paramenter, $M^{1/2}$ $Tc/Pc^{2/3}$ $Vc^{5/6}$

**Subscript**

C critical constant
R reduced variable

**Superscript**

* dilute gaseous state

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