Thermal Conductivity in the Gas Critical Region II

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Abstract

We have studied the thermal conductivity by extracting the most dominant part due to the critical fluctuation of the critical value involved in the continued fraction expansion which determined by the static correlation functions. To study most dominant part, we assumed the static scaling laws for the static correlation fluctuations with small wave numbers. This permits the estimation of the critical index of the thermal conductivity near the critical point. Our result is in agreement with experimental results.

§ 1. Introduction

In the preceding paper[1] (hereafter referred to as I ) we presented a theory of the thermal conductivity exhibiting anomalous peaks near the critical point employing the continued fraction expansion which determined by the static correlations. In the present paper we calculated the static correlation functions and we determined the temperature dependence of the thermal conductivity and the Rayleigh line width above T_c.

Before calculating the static correlation functions and determining the temperature dependence of the thermal conductivity, we show the results the continued fraction expansion of the anomalous part of the thermal conductivity \( \Delta \lambda \), which is

\[
\Delta \lambda = \frac{1}{k_B T} \lim_{k \to 0} \frac{1}{r_n} \sum_{q, q'} M_{qq'}^{(0)} \left( \frac{1}{k_B T} \frac{1}{r_n} \sum_{q, q'} M_{qq'}^{(0)} \left( \frac{1}{k_B T} \frac{1}{r_n} \sum_{q, q'} M_{qq'}^{(0)} \right) \right)
\]

(1.1)

(\( k_B \) is the Boltzmann constant, \( T \) absolute temperature, \( V \) the total volume and \( N \) the total particles number) where the numerators are written by

\[
M_{qq'}^{(0)}(q, q') = g_c(q)g_c(q')\left< A_q^* A_{q'}^* \right>
\]
\[ M^{(a)}_{rr';qq'}(k) = g^{(a)}_{r} g^{(a)}_{q'} \frac{\langle A^{*}_{a} A^{*}_{a} \rangle}{\langle A^{(a)}_{a} A^{(a)}_{a} \rangle}, \]  

where

\[ g_{a} = \lim_{q \to 0} \frac{\langle J_{n_{a}} A^{*}_{a} \rangle}{\langle |A^{(a)}_{a}|^{2} \rangle}. \]  

(1.3)

Other expressions and notations are shown in (1).

§ 2. Static correlation functions

We first calculate the correlation function \( \langle A^{*}_{a} A^{*}_{a} \rangle \), which \( A^{*}_{a} \) is written by, in (1),

\[ A^{*}_{a} = n_{a} j_{a} \rightarrow \sum \frac{n_{a} j_{a} \langle j_{a}^{*} \rangle}{\langle j_{a}^{*} j_{a} \rangle} j_{a}. \]  

(2.1)

In classical statistics the probability distribution for the coordinates and for the momenta are independent of each other. Hence one can average over the momenta by an overline and using the formula\(^{2}\)

\[ \overline{P_{i} P_{j}} = m g T \delta_{j_{a}, j_{a}} \delta_{j_{a}, j_{a}} \]  

we obtain

\[ \overline{j_{i} j_{i}^{*}} = \delta_{j_{a}, j_{a}} \left( \frac{k_{B} T}{m} \right) n_{j_{a} - j_{a}^{*}}. \]  

(2.3)

Thus (2.1) can be written as

\[ A^{*}_{a} = n_{a} j_{a} \rightarrow S(q) j_{a}, \]  

(2.4)

where

\[ S(q) = \langle n_{a} n_{a} \rangle / N \]  

(2.5)

Use of (2.3) yields

\[ \langle A^{*}_{a} A^{*}_{a} \rangle = \delta_{j_{a}, j_{a}} \left( \frac{k_{B} T}{m} \right) n_{j_{a} - j_{a}^{*}} n_{j_{a} - j_{a}^{*}} - NS(q) S(q'). \]  

(2.6)

The static scaling laws\(^{3,4}\) imply that the multiple correlations of number density have the form

\[ \langle n_{q_1} n_{q_2} \cdots n_{q_s} \rangle \sim \kappa^{3-s} f(q_1 / \kappa, \cdots, q_s / \kappa), \]  

(2.7)

where \( \kappa \) is a constant determined by critical indexes.

Using this result, we find asymptotically that

\[ \langle A^{*}_{a} A^{*}_{a} \rangle = \left\{ \begin{array}{ll}
\delta_{j_{a}, j_{a}} \left( \frac{k_{B} T}{m} \right) N^{2} S(q) \left( 1 - \frac{1}{N} S(q) \right) & \\
\sim N^{2} \kappa^{3-s} f(q / \kappa) & \text{for } q = q', \\
\delta_{j_{a}, j_{a}} \left( \frac{k_{B} T}{m} \right) \langle n_{q_1} n_{q_2} \cdots n_{q_s} \rangle - NS(q) S(q') & \text{for } q \neq q',
\end{array} \right. \]  

(2.8)

where \( \langle \cdots \rangle \) denotes the cumulant average.

Next we shall consider the coefficient \( g_{a} \). In order to calculate \( g_{a} \) we first consider

\[ ik^{*} g^{(a)}(q) = \sum_{j_{a}} \langle j_{a}^{*} A^{*}_{a} \rangle \left[ A^{(a)}_{a} A^{(a)}_{a} \right]^{-1} j_{a}, \]  

(2.9)

where \( \langle A^{(a)}_{a} A^{(a)}_{a} \rangle \) are the \( (\mu, \nu) \) elements of the inverse matrix of \( \langle A^{(a)}_{a} A^{(a)}_{a} \rangle \), which consists of the \( A^{*}_{a} A^{*}_{a} \) elements. Noting that the diagonal elements have the dependence of \( N^{2} \kappa^{3-s} \) and the nondiagonal elements
have the dependence of $N \kappa^{3-3z}$, we obtain as $N \to \infty$,

$$\det \langle A_{1h} A_{1h}^* \rangle = \Pi \Pi < |A_{1h}^*|^{2} >, \quad (\mu = x, y, z). \quad (2.10)$$

Thus the diagonal elements and nondiagonal elements of the inverse matrix of $\langle A_{1h} A_{1h}^* \rangle$ turn out to be, respectively,

$$b_{\rho, \sigma, \rho} = \frac{1}{< |A_{1h}^*|^{2} >} \sim N^{-2} \kappa^{-3+3z},$$

$$b_{\rho, \sigma, \sigma} = \frac{< A_{1h} A_{1h}^* >}{< |A_{1h}^*|^{2} >} < |A_{1h}^*|^{2} > \sim N^{-3} \kappa^{-3+3z}. \quad (2.12)$$

Use of $\langle AB \rangle = -\langle AB \rangle$ and $(P_{q})^2 = P_{q}^2$ leads

$$\langle f_{1}^* A_{1h}^* k^{*} \rangle = \langle \hat{A}_{1h}^* A_{1h}^* k^{*} \rangle = -\langle A_{1h}^* \hat{A}_{1h}^* k^{*} \rangle, \quad (2.13)$$

where

$$\hat{A}_{1h}^* = \sum_{q} i k \cdot \frac{1}{m} [n_{q} \Pi_{q}^{*} \varepsilon_{q} - S(q) \Pi_{q}^{*} \varepsilon_{q}]$$

$$+ \sum_{q} [\langle i q k^{*} \rangle - \frac{1}{m} n_{q} \Pi_{q}^{*} \varepsilon_{q}], \quad (2.14)$$

where $\Pi_{q}^{*}$ are the Fourier components of $(\mu, \kappa)$ stress tensor defined by

$$m_{ij} = i \sum_{p} \kappa^{*} \Pi_{ij}^{*}. \quad (2.15)$$

Now let us consider the correlation function with the stress tensor. Using (2.15) and (2.4) we have

$$i \sum_{q} k^{*} < \Pi_{q}^{*} n_{q}^{*} > = ik^{*} \kappa_{v} T \nu_{v}. \quad (2.16)$$

If we assume that $\langle \Pi_{q}^{*} n_{q}^{*} \rangle$ are homogeneous function of $k$ and $\kappa$ for the small values of $k$ and $\kappa$, we have

$$\langle \Pi_{q}^{*} n_{q}^{*} \rangle = C \kappa_{v} T \nu_{v}, \quad (2.17)$$

where $C$ is some constant $u$ for $\nu = \mu$ and some constant $v$ for $\nu = \mu$ and $u$ and $v$ satisfy the relation $u + v = 1$. Similarly we obtain

$$\langle \Pi_{q}^{*} \nu_{v} \rangle = C \kappa_{v} T \nu_{v}. \quad (2.18)$$

From (2.14) and (2.15), we have

$$\langle n_{q} \Pi_{q}^{*} n_{q}^{*} \rangle = C \frac{V}{m} \left( \frac{\partial n}{\partial \mu} \right)_{T, \nu} = C V \left( \frac{n}{\mu} \right)_{T}^{*} \chi_{T}, \quad (2.19)$$

$$\langle H n_{q} \Pi_{q}^{*} n_{q}^{*} \rangle = C \frac{V}{m} \left( \frac{\partial (nh)}{\partial \mu} \right)_{T, \nu}$$

$$= C \frac{V}{m} \left[ n^{*} h \chi_{T} + n(1 - T \alpha_{T}) \right], \quad (2.20)$$

where $\beta = 1/k_{B} T$ and use has been made of the hydrodynamic relations

$$\left( \frac{\partial n}{\partial \mu} \right)_{T, \nu} = \chi_{T} n^{*}, \quad (2.21)$$

$$\left( \frac{\partial h}{\partial \mu} \right)_{T, \nu} = (1 - T \alpha_{T}), \quad (2.22)$$

where $\alpha_{T}$ is the coefficient of thermal expansion at constant pressure. Thus we have, for the small values of $k$ and $\rho$, from (2.19) and (2.20)

$$\langle A_{1h} n_{q} \Pi_{q}^{*} n_{q}^{*} \rangle = C \frac{V}{m} n(1 - T \alpha_{T})$$
\[ \alpha_T = \frac{n}{1} x_T (C_v - C_T), \]  
where use has been made of fact that from the thermodynamic relation \(^2\)

\[ n_a T = T(C_p - C_v) \]

the \( \kappa \) dependence of \( \alpha_T \) is proportional to \( \kappa^{-2\alpha} \).

Similarly we obtain, for small value of \( k \) and \( q \),

\[ \langle \Delta k I^2 \sigma^m \rangle = 0, \]  
\[ \langle \Delta k (\sigma^m \sigma^m) \rangle = 0. \]

Therefore, from (2.13), (2.14), (2.23), (2.25), and (2.26), we obtain

\[ \frac{1}{\kappa^2} \langle f_{\kappa}^2 \Lambda^* \rangle = \kappa^{-2\alpha} N f(k/\kappa, q/\kappa). \]

Use of (2.13), (2.21), (2.25), and (2.27) yields

\[ g_{\sigma}(q) = \kappa^{-2\alpha} N \sum f(k/\kappa, q/\kappa) \frac{\langle \Lambda_{\sigma k} \Lambda_{\sigma k} \rangle}{\langle \Lambda_{\sigma k}^2 \rangle \langle \Lambda_{\sigma k}^2 \rangle} \]

\[ = \frac{1}{N} f_0(k/\kappa, q/\kappa) + \kappa^{(\alpha+\frac{1}{2})} \partial_{\kappa,\sigma}. \]

Thus, we obtain

\[ g_{\sigma} \approx \frac{1}{N} f_0(k/\kappa, q/\kappa). \]

Using (1.2), (2.30), and (2.8) we have asymptotically

\[ M^{(\sigma)}(qq', k) \approx \delta_{\kappa,\sigma} \delta_{q,\sigma} N^\alpha \kappa^{-2\alpha} f(k/\kappa, q/\kappa). \]

Next let us consider the \( l \)-th numerator \( M^{(l)} \) \( (l = 2, 3, \ldots) \) defined by

\[ M^{(l)} = \left\{ \begin{array}{ll}
M^{(2m, m)} = g^{(2m)}(q_{1,1} \ldots q_{1, m}) \frac{\langle \Lambda_{1,1} \Lambda_{1,1} \rangle}{\langle \Lambda_{1,1}^2 \rangle \langle \Lambda_{1,1}^2 \rangle} 
& \text{for } m = 1, 2, \ldots, \\
M^{(2m-1, m-1)} = g^{(2m-1)}(q_{1,1} \ldots q_{1, m-1}) \frac{\langle \Lambda_{1,1} \Lambda_{1,1} \rangle}{\langle \Lambda_{1,1}^2 \rangle \langle \Lambda_{1,1}^2 \rangle} 
& \text{for } m = 2, 3, \ldots,
\end{array} \right. \]

where

\[ g^{(2m)}(q_{1,1} \ldots q_{1, m}) = \sum_{q_{1,1} \ldots q_{1, m}} \langle f^{(2m-1)} A^{(2m)}(q_{1,1} \ldots q_{1, m}) \rangle \cdot \langle \Lambda^{(2m)}(q_{1,1} \ldots q_{1, m}) \rangle, \]

\[ g^{(2m-1)}(q_{1,1} \ldots q_{1, m}) = \sum_{q_{1,1} \ldots q_{1, m}} \langle f^{(2m-1)} A^{(2m-1)}(q_{1,1} \ldots q_{1, m}) \rangle \cdot \langle \Lambda^{(2m-1)}(q_{1,1} \ldots q_{1, m}) \rangle, \]

where \( f^{(i)} \) denotes the \( i \)-th random force. We take \( A^{(2m)} \) and \( A^{(2m-1)} \) as, respectively,

\[ A^{(2m)}(q_{1,1} \ldots q_{1, m}) = (1 - \sum_{i} N_{i,1} \ldots N_{i, m}) \left( \prod_{j} n_{q_{1,1} \ldots q_{1, m}}^{(m)} \right), \]

\[ A^{(2m-1)}(q_{1,1} \ldots q_{1, m}) = (1 - \sum_{i} N_{i,1} \ldots N_{i, m}) \left( \prod_{j} n_{q_{1,1} \ldots q_{1, m}}^{(m)} \right), \]

where \( P_{i} \) denotes the projection operator into subspace spanned by \( [A^{(i)}] \).

Taking the sum of the \((l - 1)\)-th denominator of (1.1) the projection parts onto lower order \( A^s \) in the static correlation \( \langle A^{(1)} A^{(1)} \rangle \) and \( \langle f^{(l-1)} A^{(1)} \rangle \) always yield negligible contribution as \( N \to \infty \) and \( \kappa \to 0 \). The static correlation of any of \( A^s \) has only one term which contributions to the corresponding
sum, and this term is the diagonal part of the matrix $\langle A^{(1)} A^{(1)*} \rangle$ which consists of a product of the pair correlations of $n_\alpha$ after expanding the static correlation by the cumulant averages. In that case, if the number of $n_\alpha$ in the static correlation is odd, that term consists of a product of $N$ and the pair correlations of $n_\alpha$. Thus we can write them as follows;

$$
\langle A^{(2m)} A^{(2m)*} \rangle \sim \kappa^{-2(m+1)} e^{(N \kappa^3)^m \prod \delta q_i q_j} \delta q_{m+1},
$$

$$
\langle A^{(2m-1)} A^{(2m-1)*} \rangle \sim \kappa^{-2m} e^{(N \kappa^3)^{m-1} \prod \delta q_i q_j}. \tag{2.34}
$$

In the case of the static correlation $\langle f^{(1)} A^{(1)} \rangle$, only one term which contributes to the corresponding sum consists of a product of $N$ and the pair correlations of $n_\alpha$ if $I=2m$, or a product of $N$ and one triple correlation if $I=2m-1$. We can write then as

$$
\langle f^{(2m-1)} A^{(2m-1)*} \rangle \sim \kappa^{-2m} N(N \kappa^3)^m \prod f_m,
\langle f^{(2m-1)} A^{(2m-1)*} \rangle \sim \kappa^{-2m} N(N \kappa^3)^{m-1} f_{m-1}, \tag{2.35}
$$

where $f_m$ and $f_{m-1}$ contain $m$ and $m-1$ Kronecker's delta.

Therefore, from above results, we obtain

$$
\langle f \rangle = \kappa^{-2} \int \frac{m^{(1)}(s, k/\kappa)}{s + \kappa^{-1} + 2s} \frac{m^{(2)}(s, k/\kappa)}{s + \kappa^{-1} + 2s} ds,
\langle f \rangle = \kappa^{-2} \int \frac{m^{(1)}(s, k/\kappa)}{s + \kappa^{-1} + 2s} \frac{m^{(2)}(s, k/\kappa)}{s + \kappa^{-1} + 2s} ds. \tag{2.36}
$$

where $m^{(i)}$ denotes $M^{(i)}$ divided by the value of $\kappa$ and $N$ of it.

Eq. (2.37) leads to the $\kappa$ dependence of the form

$$
\lambda \sim \kappa^{\frac{1}{2} - \frac{3}{2} \eta}. \tag{2.37}
$$

This result agrees with our previous work.\(^5\)

§ 3. Experimental results

Many of the thermodynamic properties of systems in the critical region are found to exhibit simple power-law dependences on the reduced differential temperature $\varepsilon=(T-T_0)/T_\infty$. Above the critical temperature on the critical isochore the specific heat at constant pressure $C_p$, which diverges in the same way as the isothermal compressibility $x_T$, is proportional to $\varepsilon^{-\gamma}$, while the thermal conductivity $\lambda$ is proportional to $\varepsilon^{-\psi}$. Therefore, the thermal diffusivity $\chi=\lambda x_T$ is proportional to $\varepsilon^{-\psi}$. Recently three groups have reported the measurements of the thermal diffusivity of CO$\_2$. The classical thermodynamic measurements of the thermal diffusivity of CO$\_2$ yields the exponent $\gamma-\psi=0.78$ for the temperature range $1.06\leq T-T_\infty\leq44^\circ C$. Seigel and Wilcox\(^6\) have given $\gamma-\psi=0.7\pm0.1$ for $0.0033\leq T-T_\infty\leq0.020^\circ C$. Recent line width measurements by Osmundson and White\(^7\) have given $\gamma-\psi=\%$. The results by Swinney and Cummins\(^8\) have found $\gamma-\psi=0.73\pm0.02$ for $0.0033\leq T-T_\infty\leq44^\circ C$.

Noting that $\gamma=2-\eta$ and (2.37), our result for $\gamma-\psi$ with the expected temperature dependence of the thermal diffusivity yields
Next let us consider that \( \kappa \sim \varepsilon^\nu \) on the critical isochore as \( \varepsilon \to 0 \). These are no data for \( \nu \) in pure fluids. For ferromagnets \( \nu = \frac{2}{3} \) and for Ising model \( \nu = 0.643 \pm 0.003 \). Thus we would employ the accept value \( \nu = \frac{2}{3} \). If we also that \( \nu \) for ferromagnets \( \nu = 0.07 \pm 0.07 \), our result is in reasonable agreement with the data from the experiments cited above.

Kadanoff and Swift\(^4\) have extended scaling-law techniques to the determination of transport coefficients near the critical point. They predict that \( \lambda \sim nC_p\kappa \), so that \( \chi = \lambda/nC_p \sim \kappa \). Using time-dependent correlation functions obtained by assuming that the free energy depends quadratically on the density gradient, Fixman\(^5\) calculates that on the critical isochore, \( \Delta\lambda \sim \kappa^{-1} \), where \( \lambda = \lambda_0 + \Delta\lambda \), and \( \lambda_0 \) and \( \Delta\lambda \) are, respectively, the temperature independent and anomalous parts of the thermal conductivity. Mountain and Zwanzig\(^{10}\) have also obtained \( \Delta\lambda \sim \kappa^{-1} \) in a calculation of thermal conductivity for a van der Waals gas using the time correlation function method. Our result is also in agreement with their results.

References