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Abstract

A theory is presented for the thermal conductivity exhibiting anomalous peaks near the critical point employing the continued fraction expansion which determined by the static correlations and introduced the irreversible character.

§ 1. Introduction

By examining the spectrum of light scattering by a fluid it is possible to obtain very accurate information about the thermal fluctuations within the system. Such experiments are of interest because they provide a method of proving the dynamic behavior of a many-body system on a scale which is not available by any other means. Light-scattering experiments are particularly useful near the critical point where experiments are very difficult, because they are a way to measure transport properties of the fluid without imposing any sort of gradient on the system. This make it much easier to maintain thermal equilibrium during the experiment.

According to the Landau-Placzek theory,\(^1\)\(^-\)\(^2\) the ratio of the intensity of the central line (or Rayleigh component) to that of the Brillouin doublets should behave as \(C_p/C_V-1\), where \(C_p\) and \(C_V\) are the constant pressure and the constant volume specific heat per molecule, respectively. Because of the strong divergence of \(C_p\) near the critical point, this implies that the central component should dominate as the critical temperature \(T_c\) is approached. This is indeed what is observed. The half-width at half-power of this central component is predicted to vary as \(\Gamma_v\propto(\lambda/nC_p)k^2\), where \(\lambda\) and \(n\) are the thermal conductivity and the number density, respectively. If the scattering is observed at an angle \(\theta\), then a \(k\) value is given by \(k=(4\pi n_o/\lambda \phi)\sin(\theta/2)\), where
\( \lambda \) is the incident light wavelength and \( n \) the index of refraction of the scattering medium. The first measurements of the Rayleigh line width near the gas-liquid critical point were reported by Ford and Benedek for sulfur hexafluoride.\(^3\) Their self-beating technique is presently used by several investigations to study the central component near the critical point. Recently three groups have reported that the Rayleigh line width of \( \text{CO}_2 \) vanish as \((T-T_c)^{-2/3}\) above the critical temperature.\(^4\)–\(^6\) In this paper, we have studied theoretically thermal conductivity and the Rayleigh component width in the critical gases with the use of the generalized continued expansion\(^7\) of the thermal conductivity.

In §2 we formulate the thermal diffusion mode of one-component fluids with the aid of a theory of generalized Brownian motion. In §3 we extract the most dominant terms from the heat flux in the time correlation function of the thermal conductivity and expand the time correlation function of the thermal conductivity in the form of a generalized-continued fraction. Thus the thermal conductivity is expressed in terms only of the static correlation functions.

§2. Thermal diffusion mode of one-component fluids

with the aid of a theory of generalized Brownian motion presented by Mori\(^8\) we first formulate the width of the central line on a more rigorous basis. A general equation of motion for a set of dynamical variable \( A(t) \) takes the form

\[
\frac{d}{dt} A(t) - i\hat{\omega} A(t) + \int_0^t \varphi(t-s) A(s) ds = f(t),
\]

where \( \hat{\omega} \) is a frequency matrix determining the collective oscillation of \( A(t) \), and is given by

\[
i\hat{\omega} = \langle \hat{A} \hat{A} \rangle - \langle AA^* \rangle^{-1} \langle AA^{*e} \rangle,
\]

where the angular brackets denote the average over the equilibrium ensemble, thus \( \langle FG^{*e} \rangle \) representing the correlation function of \( F \) and \( G \). The random force \( f(t) \) consists of those terms which are either non-linear in \( A(s) \), \( t \geq s \geq 0 \), or dependent on the other degrees-of-freedom explicitly, and its time-correlation function is connected with the damping function \( \varphi(t) \) by

\[
\langle f(t_1) f(t_2)^* \rangle = \varphi(t_1-t_2) \langle AA^* \rangle.
\]

In terms of the projection operator

\[
PG = \langle GA^* \rangle - \langle AA^* \rangle^{-1} A,
\]

the random force \( f(t) \) is defined by

\[
f(t) = e^{(t-\tau)\hat{L}H} (1 - P) \hat{A},
\]

where \( L \) is the Liouville operator, thus \( iLH \) denoting the Poisson bracket \( \{H, G\} \), where \( H \) is the hamiltonian of the system. Thus the projection of \( \hat{A} \) onto the \( A \) axis is equal to \( i\hat{\omega} A \), and its vertical component is given by
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$f(0)$. Equation (2.1) is an exact equation motion and is valid for an arbitrary dynamical variable. If the correlation time of the random force $\tau$ is very short compared to the relaxation time of $A(t)$, then we can neglect the memory effect in (2.1) and obtain, for $t \gg \tau$,

$$\frac{dA(t)}{dt} - i\omega \cdot A(t) + \Gamma \cdot A(t) = f(t), \quad (2.6)$$

where

$$\Gamma = \int_0^\infty \varphi(t) \cdot e^{-t^2} dt. \quad (2.7)$$

Let us now take as $A_\alpha$ the orthogonal set of dynamical variables

$$A_\alpha = [a_\alpha] = \begin{pmatrix} n_k \\ j_k \\ H_k - g_k n_k \end{pmatrix}, \quad (2.8)$$

where $n_k$, $j_k$, and $H_k$ are the Fourier components of the number density, the momentum density, and the energy density with wave vector $k$, respectively. $g_k$ is defined by

$$g_k = \frac{\langle H_k n_k \rangle}{\langle n_k n_k \rangle}. \quad (2.9)$$

The set of variables (2.8) is complete set for the description of the hydrodynamic motion of fluids. This is based on the fact that this set of variables are the only conserved quantities of fluids and thus their relaxation times become very long as the wave number $k$ gets small. Due to this kinematical slowing-down, the relaxation times of (2.8) are long compared to the correlation times of their random forces so that we can employ the long time approximation (2.6) and (2.7). In the light scattering we can use this long time approximation even in the vicinity of the critical point, since the scattering wave number $k$ and the energy loss are still small compared to the characteristic wave number and frequency of the fluid. At the critical point, however, this long time approximation would break down and the memory effect would be important just as in the magnetic critical point.

Let us now consider the line width of the Rayleigh line. The normal coordinate of the Rayleigh line is given by

$$A_\alpha^r = H_k - n_k h, \quad (2.10)$$

where $h$ is the enthalpy per molecule. This normal coordinate has no frequency, and its damping constant is given by

$$\Gamma^r = \frac{1}{\langle A_\alpha^r A_\alpha^r \rangle} \int_0^\infty \langle f_\alpha(t) f_\alpha^* \rangle dt, \quad (2.11)$$

in terms of the corresponding random force $f_\alpha(t)$. With the aid of the conservation laws of energy and number density,

$$\dot{H}_k = i k \cdot j_k, \quad \dot{n}_k = i k \cdot j_k, \quad (2.12)$$

we find that

$$f_\alpha^r = \langle 1 - P_k \rangle A_\alpha^r = i k \cdot J_k, \quad (2.13)$$
where
\[ J_{\gamma k} = (1 - P_k)(j_{\gamma k} - h_{\gamma k}) = (1 - P_k)j_{\gamma k}. \] (2.14)

The projection operator \( P_k \) in (2.13) and (2.14) represents the projection into the subspace spanned by the set of variables (2.8). Since the projection (2.4) is invariant under any linear transformation of the variables \( \hat{A}_k \), we can use (2.4) with \( \hat{A}_k \) as \( A \) even if we are now working in terms of the normal coordinates. In (2.14) we have used that \( P_k j_k = h_k \). It is also interesting to note that \( P_k h_k = h_k \). Since \( \left< A_{\mu}^2 \right> = N k_B T C_\mu \), (2.11) can be thus written in the following form:
\[ r_\gamma = \left( k^2 / n C_\mu \right) \lambda, \] (2.15)
where
\[ \lambda = \frac{1}{k_B T^2} \lim_{k \to 0} \lim_{t \to \infty} \frac{1}{V} \int_0^\infty \left< J_{\gamma k}(t) J_{\gamma k}^* \right> dt, \] (2.16)
where the superscript \( \mu \) means one of the \( x, y, \) and \( z \) components of the vector. It should be noted here that the correlation of the random force \( f_{\gamma k}^*(t) \) or \( J_{\gamma k}(t) \) with those of the other normal modes can be neglected in the approximation up to the order of \( k^2 \). Therefore (2.15) provides us with the half line width of the Rayleigh line correctly in the limit of the small scattering wave number \( k \).

§ 3. Thermal conductivity

In order to study the anomaly in the thermal conductivity \( \lambda \) near the critical point, we have to extract the most dominant part due to the critical fluctuation of the critical variables involved. As noted just after (2.1) and discussed in detail in the reference 8), the random force \( f_{\gamma k}^* \) or \( J_{\gamma k}(t) \) consists of the non-linear terms with respect to the macroscopic variables \( A_k \) and the force \( F_k \) which explicitly depends on the microscopic degree-of-freedom. Namely,
\[ J_{\gamma k} = (1 - P_k)\left( \sum_{q \neq k} \sum_{m} g_{\gamma q}^m a_{\gamma m}^* a_{\gamma m} \right. \]
\[ + \sum_{q \neq k} \sum_{n} \sum_{m} g_{\gamma q n} a_{\gamma m}^* a_{\gamma n} a_{\gamma q} a_{\gamma q}^* + \cdots \left. + F_k \right), \] (3.1)
where \( \sum_{q \neq k}, \sum_{n}, \) etc. denote the summation over all the macroscopic variables (2.8). The projection \( (1 - P_k) \) has been operated in order to insure that each term thus obtained is orthogonal to these macroscopic variables. In the wavelength limit, we have\(^8,9\)
\[ \left< f_{\gamma k}^2 \right> = N k_B T / m, \quad \left< n_k \right> = N k_B T n_x, \] (3.2)
\[ \left< H_k - g_{\gamma n} n_k \right> = N k_B T^2 C_r, \] (3.3)
\[ \left< H_k - h_{\gamma n} n_k \right> = N k_B T^2 C_r. \] (3.4)

In the critical region, the isothermal compressibility \( \chi_T \) is strongly divergent with the critical exponent \( \gamma \sim 4/3 \),\(^{10}\) whereas the constant volume specific heat \( C_r \) shows only a weak divergence with the critical exponent \( \alpha \sim 0.10\).
In the following, therefore, we neglect the anomaly in $C_V$ and regard the number density $n_k$ as the only critical variable. Thus we are interested in the terms of (3.1) which have the number density $n_k$. Among them we first consider the bilinear terms $n_k n_{-q}$. In order to extract such bilinear terms completely, we introduce the column matrix

$$\hat{A}_{1k} = [(1 - P_k) n_{q_{-q}}],$$

(3.5)

which consists of the difference $\mu$ and $q$ components. Denoting by $P_{1k}$ the projection operator into the subspace spanned by (3.5), we have

$$J_{1k} = P_{1k} J_{1k} + (1 - P_{1k}) J_{1k},$$

(3.6)

where the first part takes the form

$$P_{1k} J_{1k} = \langle J_{1k} \hat{A}_{1k} \rangle \cdot \langle \hat{A}_{1k} \hat{A}_{1k} \rangle^{-1} \cdot \hat{A}_{1k} \cdot \langle 1 - P_k \rangle n_{q_{-q}}.$$  

(3.7)

Since the system is isotropic, the coefficients of (3.7) should be of the form

$$g^{+}(q) = \frac{1}{4} \left[ g_0(q^2) \delta_{n+q^2} + q^2 q^4 g_1(q^2) \right].$$

(3.8)

Near the critical point the fluctuations with small wave numbers become important and the most dominant contribution will come from the first term of (3.8). Thus separating the bilinear terms with small wave numbers, we obtain

$$J_{1k} = \frac{1}{N} g_0(\varphi^2) \hat{A}_{1k} + J_{1k},$$

(3.9)

where

$$A_{1k} = (1 - P_k) n_{q_{-q}}.$$  

(3.10)

The coefficient $g_0$ is given by

$$g_0 = \lim_{q \to 0} \lim_{\lambda \to 0} \frac{1}{N} \sum_{q} \left\langle A_{1k}(t) A_{1k}^{**} > \right\rangle e^{-\epsilon t} dt,$$  

(3.11)

where $\epsilon$ is a positive number and will be set to be zero after some transformation. The time evolution of $A_{1k}(t)$ is governed by the same evolution operator as the random force (2.5);

$$A_{1k}(t) = \exp (i L_{k} t) A_{1k},$$

(3.12)

$$L_k = (1 - P_k) L.$$  

(3.13)

In order to know $\langle A_{1k}(t) A_{1k}^{**} >$ in more detail, we apply the continued-fraction-expansion to its Laplace transform. Since the evolution operator $iL_k$ is the linear operator, we can obtain

$$\int_0^\infty \langle A_{1k}(t) A_{1k}^{**} > e^{-\epsilon t} dt = \frac{\langle A_{1k}^{**} A_{1k}^{**} >}{z - i \omega_{k} - \varphi_{k}}.$$  

(3.14)
The random force \( f^*_r(t) \) is defined by
\[
f^*_r(t) = \exp[C(1-P^*_r)I]L_k \exp[C(1-P^*_r)I]A^*_r,
\]
with the aid of the projection operator
\[
P^*_r G = \langle gA^*_r A^*_r \rangle / \langle gA^*_r A^*_r \rangle. \tag{5.19}
\]
which satisfies the relation \((P^*_r)^2 = P^*_r.\)

Next from the nonlinear terms with respect to the macroscopic variables in the expansion of \( iL A^*_r \) we extract the next lowest terms which are dominant and satisfy the time reversal. For such terms we introduce the column matrix
\[
A_{2r} = \langle (1-P^*_r)(1-P^*_r) n,n_{2r} \rangle. \tag{5.20}
\]
which consists of the different \((n, n_{2r})\) pair components.

Denoting by \( P_{2r} \) the projection operator into the subspace spanned by \( (n, n_{2r}) \), we have
\[
f^*_r = P_{2r}f^*_r + (1-P_{2r})f^*_r, \tag{5.21}
\]
where the first part takes the form
\[
P_{2r}f^*_r = \langle f^*_r A_{2r} \rangle \cdot A_{2r}^{-1} \cdot A_{2r} = \sum_{r'} g^*_r A^*_r, \tag{5.22}
\]
where
\[
A^*_r = (1-P^*_r)(1-P^*_r) n,n_{2r}, \tag{5.23}
\]
and
\[
g^*_r = \sum_{r'} \langle f^*_r A^*_r \rangle \cdot \langle A_{2r} A^*_r \rangle^{-1} \cdot r', r'. \tag{5.24}
\]

The time evolution of \( A_{2r}^*(t) \) is governed by
\[
A_{2r}^*(t) = \exp(iL_t A_{2r}^*), \tag{5.25}
\]
Thus we can also proceed in the same way as \( (5.15) \) and obtain
\[
\varphi^*_r(z) = \frac{1}{z-i \omega^*_r + \varphi^*_r(z)} \tag{5.26}
\]
where
\[
i \omega^*_r = \langle (1-P^*_r)(1-P^*_r) A_{2r}^* A_{2r}^* \rangle / \langle A_{2r}^* A_{2r}^* \rangle, \tag{5.27}
\]
and
\[
\varphi^*_r(z) = \langle f^*_r(z) f^*_r(z) \rangle / \langle A_{2r}^* A_{2r}^* \rangle. \tag{5.28}
\]

Proceeding in this manner, we obtain a continued fraction expansion of \( \Delta \lambda \), with has the form
\[
\Delta \lambda = \lim_{k \to \infty} \frac{1}{M_{00}(q; q, \lambda)} \sum_{q} M_{00}(q, q, q'; \lambda) \tag{5.29}
\]
Explicit expressions for the numerators can be written down easily, for instance,
\[
M_{00}(q, q'; \lambda) = g_c(q)g_c(q') \langle A_{2r}^* A_{2r}^* \rangle, \tag{5.30}
\]
\[
M_{rs}(r, q, q'; \lambda) = g^*_r g^*_s \langle A_{2r}^* A_{2r}^* \rangle / \langle A_{2r}^* A_{2r}^* \rangle, \tag{5.31}
\]
Since the variables \( A^*_r, A^*_r, \ldots \), are odd or even with respect to the time reversal, we have
\[
\omega^*_r = \omega^*_r \quad \ldots = 0. \tag{5.31}
\]
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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 which determined by the static correlation functions and introduced the irreversible character. This is main difference between this method and others.

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References