临界気体における体積粘性度

Bulk Viscosity in the Gas Critical Region

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(Received October 30, 1971)

Abstract

The bulk viscosity in the critical gas is studied theoretically using the theory of anomalous transport coefficients with the use of the generalized continued expansion. The anomalous increase in the bulk viscosity near the critical point is found to be much greater than that of the shear viscosity. The anomalously large sound absorption in the critical gases has been obtained as a natural extension of this result. The temperature dependence of the bulk viscosity is proportional to \((T-T_e)^{-2}\).

§ 1. Introduction

In an earlier paper\(^1\);\(^2\) we presented a theory of thermal conductivities which exhibit anomalous sharp peaks near the critical point. In the present paper we apply this theory to the study of the bulk viscosity. Although it has not been possible to measure the bulk viscosity of fluids directly, it can be observed indirectly through its large contribution to the sound coefficient.\(^3\)

§ 2. Bulk viscosity

In this section we study the bulk viscosity \(\zeta\) in the same way as the thermal conductivity. If we consider the viscosity coefficient \(\theta\) which is related to the bulk viscosity \(\zeta\) and the shear viscosity \(\nu\), we can write down the correlation expression of it as follows:\(^4\)

\[
\theta = \zeta + \frac{4}{3} \nu = \lim_{k \to 0} \lim_{V \to a} \frac{1}{k_B T V} \int_t^\infty \langle J_\tau^\tau(t) J_\tau^\tau \rangle e^{-\lambda t} dt,
\]

where

\[
J_\tau^\tau = (1 - P_\delta) \Pi_\tau^\tau = \Pi_\tau^\tau - (\frac{\partial P}{\partial n})_\tau \xi \eta + (\frac{\partial P}{\partial E})_\tau \xi \eta. \tag{2.2}
\]
\( \Pi^{\text{ex}} \) is the Fourier component of the \( x, x \) component of the stress tensor and is given by

\[
\Pi^{\text{ex}} = \frac{\pi}{V} \sum_{i=1}^{N} m_i v_i r_i^2 \left\langle \exp(ik \cdot r_i) \right\rangle \tag{2.3}
\]

where \( P_a(R) \) is defined by

\[
P_a(R) = R \frac{\partial V}{\partial R} \frac{1}{ik \cdot R} \tag{2.4}
\]

where \( v_i \) and \( m_i \) are the velocity and the mass of the \( i \)-th particle, respectively, \( r_{ij} \) the relative coordinates of the \( i \)-th and \( j \)-th particles, \( V \) the intermolecular potential, and \( p \) the pressure. The summations are over all the particles contained in the system, \( E \) is the internal energy per unit volume, and \( n \) is the number density of molecules.

Since \( J^{\text{ex}} \) is even with respect to the time reversal first we consider the bilinear terms \( n_a n_{k-q} \) among \( J^{\text{ex}} \) which consists of the non-linear terms with respect to \( A_k \)'s. In order to extract these terms we consider the column matrix

\[
\mathbf{B}_k = \mathbf{B}^\dagger_k = \mathbf{C} (1 - P_k) n_{n_k-n_{-q}} \tag{2.5}
\]

with \( q \geq k-q \).

Denoting by \( P_{1k} \) the projection operator into the subspace by (2.5), we have

\[
J^{\text{ex}} = P_{1k} J^{\text{ex}} + (1 - P_{1k}) J^{\text{ex}} \tag{2.6}
\]

where the first part takes the form

\[
P_{1k} J^{\text{ex}} = g^k \cdot \left\langle (1 - P_k) J^{\text{ex}} \right\rangle \tag{2.7}
\]

where \( g^k \) is determined from

\[
g^k = \sum_{q} \left\langle J^{\text{ex}} B^\dagger_q \right\rangle \cdot \left( \left\langle B^\dagger_k B^\dagger_q \right\rangle \right)^{-1} \tag{2.8}
\]

Let us consider \( \left\langle J^{\text{ex}} B^\dagger_k \right\rangle \) which is written as

\[
\left\langle J^{\text{ex}} B^\dagger_k \right\rangle = (1 - P_k) \left\langle \Pi^{\text{ex}}(n_{k-n_{-q}}) \right\rangle \tag{2.9}
\]

\[
= \left\langle \Pi^{\text{ex}} n_{n_k-n_{-q}} \right\rangle - \left( \frac{\partial P}{\partial n} \right)_E \left\langle n_{n_{k-n_{-q}}} \right\rangle - \left( \frac{\partial P}{\partial E} \right)_n \left\langle n_{n_{k-n_{-q}}} \right\rangle.
\]

Using the thermodynamic relation, \( (\partial P/\partial n)_E \) and \( (\partial P/\partial E)_n \) are expressed by the relations, respectively,

\[
\left( \frac{\partial P}{\partial n} \right)_E = \frac{C_P - P \alpha}{n \chi_T C_v}, \quad \left( \frac{\partial P}{\partial E} \right)_n = \frac{\alpha}{n \chi_T C_v} \tag{2.10}
\]

where \( C_P \) and \( C_v \) are the constant pressure and the constant volume specific heat per molecule, respectively, \( \alpha \) the thermal expansion coefficient \((1/V)(\partial V/\partial T)_p\) and \( \chi_T \) the isothermal compressibility \(- (1/V)(\partial V/\partial P)_T\). We shall separate \( E_k \) into two parts, one projected onto \( n_k \) and leavings,

\[
E_k = \left\langle \frac{E_{kn_{k}}}{n_{n_{k}}} \right\rangle - n_k + E_i \tag{2.11}
\]

For the long wavelength limit we have

\[
E_k = (\hbar \frac{\alpha T}{n \chi_T}) n_k + E', \tag{2.12}
\]

where we have used the relations
\[ \langle n_k \rangle = N k_B T n_x, \quad (2.13) \]

and

\[ \langle E_k n_q \rangle = N k_B T (n n_x - \alpha T), \quad (2.14) \]

where \( h \) is the enthalpy per molecule. Inserting (2.10) and (2.12) into (2.9), and then applying

\[ \alpha^2 = n x_T (C_p - C_v), \quad (2.15) \]

we obtain

\[ \langle J^{x \beta} B^{x \beta} \rangle = \langle H^{x \beta} n_{q \beta} n_{q \beta} \rangle - \frac{E^x + n C_q}{n^2 x_T C_v} \langle n_{q \beta} n_{q \beta} \rangle \]

\[ - \left( \frac{\alpha}{n x_T C_v} \right) \langle E^x n_{q \beta} n_{q \beta} \rangle. \quad (2.16) \]

Since \( E^x \) does not contain the critical variable, we may consider that the \( \kappa(\infty T / T_\infty) \) dependence of \( \langle E^x n_{q \beta} n_{q \beta} \rangle \) is proportional to \( x_T \). Thus the second term of the right hand side of (2.16) gives the most contribution to \( \langle J^{x \beta} B^{x \beta} \rangle \). We have

\[ \langle J^{x \beta} B^{x \beta} \rangle \sim N \kappa^{3-2\xi}(k/\kappa, q/\kappa). \quad (2.17) \]

Noting that we obtain the the elements of inverse matrix of \( \langle B_{\beta \beta} \rangle \) as

\[ b_{\sqrt{\sqrt{}}} \equiv \begin{cases} 1 & \langle B_{\beta \beta} \rangle \\
\frac{\langle B_{\beta \beta} \rangle}{\langle B_{\beta \beta} \rangle} & \langle B_{\beta \beta} \rangle \end{cases} \sim N^{-3} \kappa^{3-2 \xi}, \text{ for } q = q', \]

\[ \langle B_{\beta \beta} \rangle \sim N^{-3} \kappa^{3-2 \xi}, \text{ for } q \neq q'. \quad (2.18) \]

From (2.8), (2.17), and (2.18), \( g^x_{\beta} \) turns out to be

\[ g^x_{\beta} \sim N^{-3} \kappa^{3-2 \xi}(k/\kappa, q/\kappa). \quad (2.19) \]

Using the generalized continued fraction and the static scaling laws we obtain the \( \kappa \) dependence of the anomalous part of the viscosity coefficients as

\[ \Delta \sim \kappa^{-2(2\xi + 4)}. \quad (2.20) \]

This result is more rigorous one than earlier result\(^5\) and if \( r = 0 \), two results are the same value. We can also calculate the shear viscosity in the same way. However, it is found that the shear viscosity has no anomaly. Thus only the bulk viscosity has the anomalous increase near the critical point.

\section*{§ 3. Conclusion}

In summary, the first fundamental problem of the dynamic critical phenomena is to extract the most dominant part due to the critical fluctuation of the critical variables involved. In the transport phenomena, the macroscopic motion dissipates its physical quantities to the microscopic thermal fluctuations. The dissipative processes depend on the microscopic structure of the system more sensitivity than the static properties. Thus we have to extract the anomalous part due to the critical fluctuations of macroscopic scale. To
study the most dominant part, we assumed the static scaling laws for the static correlation functions with small wave numbers.

The only work known to the author which calculated the temperature dependence of transport coefficients are the papers of Fixman and coworkers\(^6\)\(^{,7}\) and the recent papers of Kawasaki and Tanaka,\(^8\) Deutch and Zwanzig,\(^9\) Kawasaki,\(^10\) Fixman,\(^11\) Zwanzig and Mountain.\(^12\) However, the latter papers may be criticized on the same grounds as the work of Fixman, since although they follow different methods the same basic ideas are used. Let us compare our results with those of Fixman. We do not agree with Fixman’s result for the shear viscosity. We find no anomaly while he finds a term which diverges as \((T - T_c)^{-\gamma}\). Fixman's method requires that a modified form of pair correlation is used to determine the shear viscosity. Fixman did not determine the bulk viscosity so no comparison with our result is possible. The result of Mountain and Zwanzig is the same temperature dependence as our result.

References