Transport Coefficients near the Liquid-Gas Critical Point*

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A perturbation theory for the determination of transport coefficients near the critical point is presented. This perturbation theory is based upon processes in which one transport mode decays into several low-wave-number modes. Scaling-law concepts are used to calculate the order of magnitude of the matrix elements and frequency denominators which appear in this theory. This permits the estimation of the order of magnitude of the transport coefficients near the critical point. In particular, this approach indicates that the thermal conductivity should diverge roughly as $(T-T_c)^{-2/3}$ on the critical isochore and coexistence curve, while the viscosity η should be either weakly divergent or strongly cusped at the critical point. On the other hand, the bulk viscosity ζ should diverge roughly as $(T-T_c)^{-2}$ for low frequencies, and as $(T-T_c)^{-2/3}$ for higher frequencies on the critical isochore near the critical point. Specific predictions are made for these quantities in terms of critical indices, and the connection between these relations and the scaling of frequencies is discussed.

I. INTRODUCTION

In several recent papers,[1–6] correlation function or equivalent response function techniques have been applied to the problem of predicting and explaining the apparent divergences in transport coefficients near the critical point.[7] The present paper is devoted to an extension of these methods and their application to the liquid-gas phase transition. The methods of analysis are purely classical, so that the work is directly relevant to classical fluids. However, most of this work deals with long-wavelength limits in which the quantum corrections are quite small. For this reason, it is hoped that the analysis here can be appropriate for either classical or quantum fluids.

Our work is very closely related to Kawasaki's[1] formulation of Fixman's[3–5] theoretical approach. There are two main differences between our methods and Kawasaki's. First, we estimate correlation functions with the aid of the "scaling-law" idea,[8–10] which has proved very successful in describing the correlations in the two-dimensional Ising model[11,12] and moderately successful in describing the three-dimensional Ising model[13] and real three-dimensional phase transitions.[14] Kawasaki and Fixman estimated correlation functions with the aid of ideas drawn from the Ornstein-Zernike[15] theory of critical correlations, and their estimates are probably less accurate than estimates drawn from the scaling-law ideas.

The second difference between this work and Kawasaki's is a matter of formalism. Kawasaki evaluates correlation functions involving currents of conserved quantities by expanding these currents in the densities of the conserved quantities. At first sight, this expansion appears to be no better justified than the analogous expansion of the energy density to second order in the order parameter[16,17] which predicts an incorrect, $(T-T_c)^{-1/2}$, divergence in the specific heat. In this paper, we construct a formal perturbation theory for transport coefficients, which turns out to be equivalent to the expansion procedure of Kawasaki. In this way, we produce a partial justification for the basic ideas used by him and by Fixman.

The next section of this paper is devoted to the development of formal techniques; the following section applies these techniques to the estimation of transport coefficients; the final section lists the conclusions of this analysis.

II. FORMULATION

A. Liouville Equation

Any nonequilibrium problem in classical statistical mechanics can be stated in terms of the Liouville equation. We employ a state notation to describe this equation. The state vector $|t\rangle$ describes the statistical

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state of the system at time t. This state is defined so that its components

$$\langle \mathbf{p}_1,\mathbf{p}_2\cdots\mathbf{p}_N,\mathbf{r}_1,\mathbf{r}_2\cdots\mathbf{r}_N|t\rangle=\langle p,r,N|t\rangle \equiv f_N(p,r,t) \quad (2.1)$$

are the probabilities for finding N particles in the system with one particle havingco ordinate $\mathbf{r}_1$ and momentum $\mathbf{p}_1$, another with coordinate $\mathbf{r}_2$ and momentum $\mathbf{p}_2$, etc. The time development of the system is described by the Liouville equation

$$\left(\frac{\partial}{\partial t}+L\right)|t\rangle=0, \quad (2.2)$$

with L having the matrix element

$$\langle p',r',N'|L|p,r,N\rangle=\sum_{\alpha=1}^{N}\left[\frac{\partial\mathcal{H}}{\partial\mathbf{p}_\alpha}\frac{\partial}{\partial\mathbf{r}_\alpha}-\frac{\partial\mathcal{H}}{\partial\mathbf{r}_\alpha}\frac{\partial}{\partial\mathbf{p}_\alpha}\right]\times\langle p',r',N'|p,r,N\rangle \quad (2.3a)$$

and

$$\langle p',r',N'|p,r,N\rangle=\delta_{N,N'}\prod_{\alpha=1}\delta(\mathbf{p}_\alpha-\mathbf{p}_\alpha')\delta(\mathbf{r}_\alpha-\mathbf{r}_\alpha'). \quad (2.3b)$$

There are two basic states which will prove to be particularly useful in our analysis. The first of these is the equilibrium state $|\rangle$ defined by

$$\langle p,r,N|\rangle=\exp\{-\beta[\mathcal{H}(p,r)-\mu N]\}/[h^{3N}N!Z(\beta,\mu)], \quad (2.4)$$

which gives the grand canonical ensemble equilibrium distribution with chemical potential μ and inverse temperature β. The second is the "summational state"

$$\langle|=\sum_N\int\left(\prod_{\alpha=1}^{N}d\mathbf{p}_\alpha d\mathbf{r}_\alpha\right)\langle p,r,N|. \quad (2.5)$$

Notice that $|\rangle$ is not the conjugate vector to $\langle|$. However, they do have a conjugate significance relative to L since

$$L|\rangle=0 \quad\text{and}\quad \langle|L=0. \quad (2.6)$$

The importance of $\langle|$ lies in its usefulness for determining averages. For example,

$$\langle|t\rangle=1$$

expresses the proper normalization of the state $|t\rangle$. The average of the physical quantity X in the state $|t\rangle$ is given by

$$\langle X\rangle_t=\langle|X_{\rm op}|t\rangle, \quad (2.7a)$$

while the average of X in the grand canonical ensemble is

$$\langle X\rangle=\langle|X_{\rm op}|\rangle. \quad (2.7b)$$

In Eq. (2.7), $X_{\rm op}$ is a diagonal matrix in the p's and r's. (In fact, the only off-diagonal matrix in our presentation is L.)

B. Operators and States

For our purposes, the important operators in the theory are the densities and currents of conserved quantities. We write[18] the number density operator as $n_{\rm op}(\mathbf{r})$, the momentum density as $\mathbf{g}_{\rm op}(\mathbf{r})$, and the energy density as $\epsilon_{\rm op}(\mathbf{r})$. For example, the matrix element of the momentum density is

$$\langle p',r',N'|\mathbf{g}_{\rm op}(\mathbf{r})|p,r,N\rangle=\sum_{\alpha=1}^{N}\mathbf{p}_\alpha\,\delta(\mathbf{r}-\mathbf{r}_\alpha)\langle p',r',N'|p,r,N\rangle.$$

The current corresponding to these densities are $\mathbf{j}(\mathbf{r})$ (number current), $\mathbf{j}^\epsilon(\mathbf{r})$ (energy current), and $\tau_{ij}(\mathbf{r})$ (stress tensor). (In cases in which it does not appear to cause confusion, we shall drop the subscripts "op" on operators.) These currents are defined by

$$\begin{aligned}-\nabla\cdot\mathbf{j}_{\rm op}(\mathbf{r})&=[L,n_{\rm op}(\mathbf{r})],\\ -\nabla\cdot\mathbf{j}^\epsilon{}_{\rm op}(\mathbf{r})&=[L,\epsilon_{\rm op}(\mathbf{r})],\\ -\nabla\cdot\tau(\mathbf{r})&=[L,\mathbf{g}(\mathbf{r})].\end{aligned} \quad (2.8)$$

Before we begin our analysis, it is useful to recall several important properties of these currents. The first is that the diagonal element of the stress tensor $\tau_{xx}(\mathbf{r})$ is, for a system at rest, the pressure operator $p(\mathbf{r})$. The second is that products of the currents have very simple momentum averages. If $\langle\ \rangle_{\rm q}$ represents a momentum average in the grand canonical ensemble,

$$\beta\langle g_i(\mathbf{r})j_k(\mathbf{r}')\rangle_{\rm q}=\delta(\mathbf{r}-\mathbf{r}')n_{\rm op}(\mathbf{r})\delta_{ik}, \quad (2.9a)$$

$$\beta\langle g_i(\mathbf{r})j_k{}^\epsilon(\mathbf{r}')\rangle_{\rm q}=\delta(\mathbf{r}-\mathbf{r}')[\epsilon_{\rm op}(\mathbf{r})+p_{\rm op}(\mathbf{r})]\delta_{ik}, \quad (2.9b)$$

$$\beta\langle g_i(\mathbf{r})\tau_{kl}(\mathbf{r}')\rangle_{\rm q}=0. \quad (2.9c)$$

Because Eqs. (2.9) are so important to us, we define a linear combination of conserved quantities with a current which has a particularly simple correlation with $\mathbf{g}(\mathbf{r})$; namely,

$$s_{\rm op}(\mathbf{r})=\frac{1}{T}\left[\epsilon_{\rm op}(\mathbf{r})-\frac{\langle\epsilon+p\rangle}{\langle n\rangle}n_{\rm op}(\mathbf{r})\right] \quad (2.10)$$

as the symbol indicates, $s_{\rm op}(\mathbf{r})$ plays a role of an entropy density. In particular, the entropy current

$$\mathbf{j}_{\rm op}{}^s(\mathbf{r})=\frac{1}{T}\left[\mathbf{j}_{\rm op}{}^\epsilon(\mathbf{r})-\frac{\langle\epsilon\rangle+\langle p\rangle}{\langle n\rangle}\mathbf{j}_{\rm op}(\mathbf{r})\right] \quad (2.11)$$

obeys

$$\beta\langle g_i(\mathbf{r})j_k{}^s(\mathbf{r}')\rangle_{\rm q}=\frac{1}{T}\delta(\mathbf{r}-\mathbf{r}')\left[\epsilon_{\rm op}(\mathbf{r})+p_{\rm op}(\mathbf{r})-\frac{\langle\epsilon\rangle+\langle p\rangle}{\langle n\rangle}n_{\rm op}(\mathbf{r})\right]\delta_{ik}. \quad (2.12)$$

The full thermodynamic average of the right-hand side of Eq. (2.12) vanishes.

[18] In this and several other regards we follow the notation of L. P. Kadanoff and P. C. Martin, Ann. Phys. (N. Y.) **24**, 419 (1963).

In the discussion of hydrodynamic phenomena, the most important states are local equilibrium states which describe situations in which the equilibrium parameters (temperature, chemical potential, and velocity) are varying slowly from point to point. To form these states, we begin with linear combinations of the densities of conserved operators: $a_i(\mathbf{r})$ with $i=1, 2 \cdots 5$. These densities are used in the form of their Fourier transforms

$$a_i(\mathbf{q})=\int d^3r\, e^{-i\mathbf{q}\cdot\mathbf{r}}a_i(\mathbf{r}).$$

The linear combinations are set up so that the "local equilibrium states"

$$\begin{aligned}|i,\mathbf{q}\rangle&=a_i(\mathbf{q})|\rangle,\\ \langle i,\mathbf{q}|&=\langle|a_i(-\mathbf{q}),\end{aligned}\tag{2.13}$$

are properly orthonormal

$$\langle i,\mathbf{q}|j,\mathbf{q}'\rangle=\delta_{i,j}(2\pi)^3\delta(\mathbf{q}-\mathbf{q}').\tag{2.14}$$

To be specific: We choose the states by writing

$$a_1(\mathbf{q})=\frac{s_{\mathrm{op}}(\mathbf{q})}{[k_B\rho C_p(\mathbf{q})]^{1/2}}.\tag{2.15a}$$

The state orthogonal to $|1,\mathbf{q}\rangle$ and properly normalized is $|2,\mathbf{q}\rangle=a_2(\mathbf{q})|\rangle$ with

$$a_2(\mathbf{q})=\frac{(\rho\beta)^{1/2}}{\langle n\rangle}c(\mathbf{q})n_{\mathrm{op}}(\mathbf{q})+\left(\frac{1}{k_B\rho}\left[\frac{1}{C_V(\mathbf{q})}-\frac{1}{C_p(\mathbf{q})}\right]\right)^{1/2}s_{\mathrm{op}}(\mathbf{q}).\tag{2.15b}$$

Finally

$$a_3(\mathbf{q})=g_x(\mathbf{q})(\beta/\rho)^{1/2},\tag{2.15c}$$

$$a_4(\mathbf{q})=g_y(\mathbf{q})(\beta/\rho)^{1/2},\tag{2.15d}$$

$$a_5(\mathbf{q})=g_z(\mathbf{q})(\beta/\rho)^{1/2}.\tag{2.15e}$$

The q-dependent "thermodynamic quantities" in Eqs. (2.15a) and (2.15b) reduce to the standard thermodynamic values at $q=0$. These are defined to have the correct value so that $a_1(\mathbf{q})$ and $a_2(\mathbf{q})$ are orthogonal and properly normalized for all q.

In particular,

$$C_p(\mathbf{q})=\langle|s_{\mathrm{op}}(-\mathbf{q})s_{\mathrm{op}}(\mathbf{q})|\rangle/k_B\rho\tag{2.16a}$$

reduces to the specific heat at constant pressure at $q=0$, while the quantities $C_V(\mathbf{q})$ and $c(\mathbf{q})$ defined by

$$C_V(\mathbf{q})[c(\mathbf{q})]^2=\frac{T\langle n\rangle}{m\rho}\frac{\langle|s_{\mathrm{op}}(-\mathbf{q})s_{\mathrm{op}}(\mathbf{q})|\rangle}{\langle|n_{\mathrm{op}}(-\mathbf{q})n_{\mathrm{op}}(\mathbf{q})|\rangle}\tag{2.16b}$$

and

$$\frac{\beta}{\langle n\rangle}c(\mathbf{q})=\frac{\left(k_B\beta\left\{\dfrac{[C_p(\mathbf{q})]^2}{C_V(\mathbf{q})}-C_p(\mathbf{q})\right\}\right)^{1/2}}{\langle|n_{\mathrm{op}}(-\mathbf{q})s_{\mathrm{op}}(\mathbf{q})|\rangle}\tag{2.16c}$$

reduce to the specific heat at constant volume and the adiabatic sound velocity at $q=0$.

In our further analysis, it will be important to make a contrast between $a_1(\mathbf{q})$ and $a_2(\mathbf{q})$. Notice that $a_1(\mathbf{q})$ as defined by Eq. (2.15a) has a normalization factor $1/\sqrt{C_p}$ while $a_2(\mathbf{q})$ has normalization factors $c(\mathbf{q})$ and $(1/C_V-1/C_p)^{1/2}$. Near the critical point, C_p diverges very strongly. For example, on the critical isochore it diverges as $(T-T_c)^{-\gamma}$, with $\gamma\approx\frac{4}{3}$. On the other hand, $1/c^2$ and C_V diverge much more weakly near the critical point, with a roughly logarithmic dependence upon $T-T_c$. Therefore, we must conclude that $a_1(\mathbf{q})$, which is proportional to the entropy density that appears in $a_1(\mathbf{q})$, has much stronger fluctuations near the critical point than the combination of operators in $a_2(\mathbf{q})$.

The point is further borne out by the thermodynamic role of the two operators within a correlation function. If we have some operator $X_{\mathrm{op}}(\mathbf{q})$ which does not depend explicitly upon the thermodynamic parameters, then

$$\lim_{q\to0}\langle|s(-\mathbf{q})X_{\mathrm{op}}(\mathbf{q})|\rangle=\beta^{-1}\left[\frac{\partial}{\partial T}\langle X\rangle\right]_p.$$

Since the condition of fixed p does not preclude any of the wild variations which occur near the critical point, these derivatives can be very large indeed. On the other hand,

$$\lim_{q\to0}\langle|a_2(-\mathbf{q})X(\mathbf{q})|\rangle\frac{\langle n\rangle}{\sqrt{(\rho\beta)}}c(\mathbf{q})=\left.\frac{\partial\langle X\rangle}{\partial\mu}\right|_{S/N}.$$

The condition of fixed S/N precisely holds constant the strongest variations which occur near the critical point. Therefore, the thermodynamic derivative at fixed S/N tends to be, at worst, weakly divergent.

The idea that there is a characteristic size to the operators a_2 and a_1 can be carried even further, to say that the addition of an extra factor of $s_{\mathrm{op}}(\mathbf{q}=\mathbf{0})$ to an expectation value, which is already undergoing critical fluctuations, multiplies this correlation function by a characteristic factor. To compute this characteristic factor notice that on the coexistence curve

$$\lim_{q\to0}\langle s_{\mathrm{op}}(-\mathbf{q})n_{\mathrm{op}}(\mathbf{q})\rangle\sim(-\epsilon)^{-\gamma};\quad \epsilon=(T-T_c)/T_c,$$

while the difference between $\langle n\rangle$ and its critical value is given by

$$|\langle n\rangle-\langle n\rangle_c|\sim(-\epsilon)^{\beta}.$$

Consequently, in this case the extra factor of s_{op} has had the effect of multiplying the thermodynamic quantity by a factor $\epsilon^{-(\beta+\gamma)}$, which diverges roughly as $(T-T_c)^{-5/3}$. In general, we expect that, for small q,

$$s_{\mathrm{op}}(\mathbf{q})\sim\epsilon^{-(\beta+\gamma)}.\tag{2.17a}$$

A similar analysis may be applied to $a_2(\mathbf{q})$. Except for the prefactor of $c(\mathbf{q})\sim1/[C_V(\mathbf{q})]^{1/2}$, a_2 acts as a temperature derivative inside a correlation function. For this reason, at small q, a_2 is of the order of

$$a_2(\mathbf{q})\sim c\epsilon^{-1}, \qquad (2.17b)$$

when it appears as a factor in an already fluctuating correlation function. On the basis of this logic, one would, for example, estimate that

$$\langle|a_2(\mathbf{q})s(\mathbf{q}')s(-\mathbf{q}-\mathbf{q}')|\rangle\sim c\frac{\partial}{\partial T}\langle|s(\mathbf{q}')s(-\mathbf{q}')|\rangle\sim c\frac{\partial}{\partial T}\epsilon^{-\gamma}$$
$$\sim c\epsilon^{-\gamma-1}$$

on the critical isochore if q and q' are very small.

This hypothesis that there is a natural size to quantities near the critical point can be extended to give an estimate of the q dependence of different correlation functions. According to the scaling hypothesis, all lengths near the critical point should be referred to a characteristic range of correlations, ξ. On the critical isochore $\xi\sim\epsilon^{-\nu}$, with $\nu\approx\frac{2}{3}$. Then, near the critical point, correlation functions like $\langle|s_{\rm op}(\mathbf{q})s_{\rm op}(-\mathbf{q})|\rangle$ and $\langle|n_{\rm op}(\mathbf{q})n_{\rm op}(-\mathbf{q})|\rangle$ should depend upon q only in the combination $q\xi$.

There is one more scaling-law result which we shall need in our arguments—a result which is much more questionable than the ones we have stated so far. The results stated above seem to give at least roughly correct estimates of divergences in the critical region; the hypothesis we are about to state has never been checked except in the two-dimensional Ising model. This extra idea is that there are essentially only two different fluctuating quantities near the critical point, e.g., $a_1(\mathbf{r})$ and $a_2(\mathbf{r})$, and that all other critically fluctuating quantities can be considered to be linear combinations of these two. As a consequence of this assumption, in its leading or most singular behavior $n_{\rm op}(\mathbf{q})$ is proportional to $s_{\rm op}(\mathbf{q})$. Hence, the ratio of correlation functions $\langle|n_{\rm op}(\mathbf{q})n_{\rm op}(-\mathbf{q})|\rangle/\langle|s_{\rm op}(\mathbf{q})s_{\rm op}(-\mathbf{q})|\rangle$ should be essentially a ratio of identical quantities so that it is very weakly dependent on either ϵ or $q\xi$ in the critical region. The product $C_V(\mathbf{q})[c(\mathbf{q})]^2$ defined by Eq. (2.16b) will then be almost a constant independent of $q\xi$ or ϵ in the critical region. This result will have important implications for sound-wave damping. However, we should point out once more that this conclusion is much less reliable than the other conclusions we have drawn from the scaling hypothesis, because this result requires the very strongest and most dubious form of that hypothesis.

C. Transport Processes

The transport modes of the system appear as slowly relaxing solutions to the Liouville equation. An eigenstate of L with eigenvalue s will relax in time as e^{-st}. Consequently, the slowly relaxing modes have a small real part to the eigenvalue s. Since L is translationally invariant, its eigenvalues may be classified according to the value of the wave number q. The transport modes appear as states whose relaxation time goes to infinity as $q\rightarrow 0$.

To find the eigenvalues of L we start with the equation for the νth right eigenstate of L corresponding to the eigenvalue s_ν:

$$s_\nu|\nu,\mathbf{q}\rangle_R=L|\nu,\mathbf{q}\rangle_R. \qquad (2.18)$$

If this is a transport eigenstate $|\nu,\mathbf{q}\rangle_R$ is mostly composed of the states $|i,\mathbf{q}\rangle$. (Notice that $\nu=1, 2\cdots\infty$ labels eigenvalues of L while $i=1, 2\cdots 5$ labels the local equilibrium states.) Then we apply $\langle i,\mathbf{q}|$ to Eq. (2.18) and find[19]

$$s_\nu\langle i,\mathbf{q}|\nu,\mathbf{q}\rangle_R=\langle i,\mathbf{q}|L|\nu,\mathbf{q}\rangle_R=\textstyle\sum_j\langle i,\mathbf{q}|L|j,\mathbf{q}\rangle \times\langle j,\mathbf{q}|\nu,q\rangle_R+\langle i,\mathbf{q}|LP|\nu,\mathbf{q}\rangle_R, \qquad (2.19)$$

where P is the projection operator which rejects the states $|i,\mathbf{q}\rangle$

$$P=1-\sum_{j=1}^{5}|j,\mathbf{q}\rangle\langle j,\mathbf{q}|. \qquad (2.20)$$

According to Eq. (2.18),

$$s_\nu P|\nu,\mathbf{q}\rangle_R=PL|\nu,\mathbf{q}\rangle_R =PLP|\nu,\mathbf{q}\rangle_R+\textstyle\sum_j PL|j,\mathbf{q}\rangle\langle j,\mathbf{q}|\nu,\mathbf{q}\rangle_R,$$

so that

$$P|\nu,\mathbf{q}\rangle_R=\frac{1}{s_\nu-PLP}\textstyle\sum_j PL|j,\mathbf{q}\rangle\langle j,\mathbf{q}|\nu,\mathbf{q}\rangle_R.$$

Thus, Eq. (2.19) can be written as

$$\textstyle\sum_j[s_\nu\delta_{ij}-L_{ij}(\mathbf{q})-U_{ij}(\mathbf{q},s_\nu)]\langle j,\mathbf{q}|\nu,\mathbf{q}\rangle_R=0, \qquad (2.21)$$

with

$$L_{ij}(\mathbf{q})=\langle i,\mathbf{q}|L|j,\mathbf{q}\rangle, \qquad (2.22)$$

$$U_{ij}(\mathbf{q},s)=\langle i,\mathbf{q}|LP\frac{1}{s-PLP}PL|j,\mathbf{q}\rangle. \qquad (2.23)$$

The eigenvalues of L are, of course, determined by the condition that the matrix $s\delta_{ij}-L_{ij}-U_{ij}$ have zero determinant.

The standard transport theory emerges from Eqs. (2.21), (2.22), and (2.23), if we identify L_{ij} with the set of thermodynamic derivatives which appear in the nondissipative part of the theory and U_{ij} with the matrix of transport coefficients appearing in the dissipative part of the theory. Once these identifications are made, we can see that Eq. (2.19) represents the usual linearized hydrodynamic equations.

To evaluate L_{ij} notice that

$$\begin{aligned}L_{ij}&=\langle i,\mathbf{q}|L|j,\mathbf{q}\rangle\\&=\langle|a_i(-\mathbf{q})La_j(\mathbf{q})|\rangle\\&=\langle|[a_i(-\mathbf{q}),L]a_j(\mathbf{q})|\rangle\\&=i\mathbf{q}\cdot\langle|\mathbf{j}_i(-\mathbf{q})a_j(\mathbf{q})|\rangle,\end{aligned} \qquad (2.24)$$

[19] In Eq. (2.19) and below, we have taken the volume of the system to be unity.

TABLE I. The matrix $(s\delta_{ij}-L_{ij}-U_{ij})$.

	Heat flow	Sound waves		Viscous flow	
Heat flow	$s-\frac{\lambda q^2}{\rho C_p}$	$-\frac{\lambda q^2}{\rho}\left(\frac{1}{C_V C_p}-\frac{1}{C_p^2}\right)^{1/2}$	0	0	0
Sound waves	$-\frac{\lambda q^2}{\rho}\left(\frac{1}{C_V C_p}-\frac{1}{C_p^2}\right)^{1/2}$	$s-\frac{\lambda q^2}{\rho}\left(\frac{1}{C_V}-\frac{1}{C_p}\right)$	$-icq_x$	0	0
	0	$-icq_x$	$s-\frac{(\zeta+\frac{4}{3}\eta)q^2}{\rho}$	0	0
Viscous flow	0	0	0	$s-\frac{\eta q^2}{\rho}$	0
	0	0	0	0	$s-\frac{\eta q^2}{\rho}$

where $\mathbf{j}_i$ is the current corresponding to the ith conserved quantity. If L_{ij} is to be nonzero, a_i must be a vector with a component parallel to $\mathbf{q}$, and a_j must be a scalar or vice versa. If $\mathbf{q}$ points in the x direction, the only possible nonvanishing elements of L_{ij} couple the scalars $(i=1,2)$ with $g_x(j=3)$ and vice versa. Furthermore, we picked the form of $a_1(q)\sim s_{\text{op}}(q)$ with the idea in mind of making

$$\langle|\,\mathbf{j}_1(-\mathbf{q})g_x(\mathbf{q})\,|\rangle\sim\langle|\,\mathbf{j}^s(-\mathbf{q})g_x(\mathbf{q})\,|\rangle=0.$$

[See Eq. (2.12).] Therefore, L_{13} and L_{31} vanish.

The only remaining terms in L_{ij} are L_{32} and L_{23}. These terms are

$$\begin{aligned}L_{32}(\mathbf{q})&=L_{23}(\mathbf{q})\\&=i\mathbf{q}\cdot\langle|\,\mathbf{j}_2(-q)a_3(\mathbf{q})\,|\rangle\\&=iq_xc(\mathbf{q})\frac{\beta}{\langle n\rangle}\langle|\,j_x(-\mathbf{q})g_x(\mathbf{q})\,|\rangle.\end{aligned}\qquad(2.25)$$

In writing the last line of Eq. (2.25), we have made use of expressions (2.15b) and (2.15c) for a_2 and a_3, and also of the fact that the entropy current $j^s(-\mathbf{q})$ can generate no contribution to the average (2.25). Equation (2.9a) now enables us to evaluate L_{23} and L_{32} and find

$$L_{23}=L_{32}=iq_xc(\mathbf{q}).\qquad(2.26)$$

If the U_{ij} in Eq. (2.23) were set equal to zero, then this hydrodynamic equation would contain two nonzero "relaxation times"

$$s_\pm=\pm icq_x,\qquad(2.27)$$

and the other three eigenvalues would be zero. These pure imaginary "relaxation times" reflect the oscillatory behavior of undamped sound waves. The vanishing of the remaining relaxation times indicates that all the diffusive processes must arise from the neglected term U_{ij}.

In fact, all the transport coefficients arise from U_{ij}. To see this, we rewrite Eq. (2.23) as

$$U_{ik}(\mathbf{q},s)=-\langle|\,\mathbf{q}\cdot\mathbf{j}_i(-\mathbf{q})P\frac{1}{s-PLP}P\mathbf{q}\cdot\mathbf{j}_k(\mathbf{q})\,|\rangle.\qquad(2.28)$$

This result has essentially the same structure as the Kubo[20] formulas for transport coefficients. It is a correlation function involving a product of currents. In place of the usual time integral, Eq. (2.28) contains a denominator with differences of relaxation times.

There are 25 terms in U_{ik}; but there are only three independent transport coefficients λ, η, ζ.

Our next task must be the elimination of redundant terms. Notice that the current for particle flow $\mathbf{j}$ is proportional to the momentum density. The projection operators eliminate this current. Hence, of the terms U_{11}, U_{21}, U_{12}, and U_{22}, there is only one independent combination: that arising from the energy current $\mathbf{j}^\epsilon$. We have

$$q^2\lambda(\mathbf{q},s)=-\langle|\,s_{\text{op}}(-\mathbf{q})LP\frac{1}{PLP-s}PLs_{\text{op}}(\mathbf{q})\,|\rangle/k_B,\qquad(2.29)$$

with the U's being given by

$$U_{11}(\mathbf{q},s)=q^2\lambda(\mathbf{q},s)/\rho C_p(\mathbf{q}),\qquad(2.30)$$

$$U_{22}(\mathbf{q},s)=q^2\lambda(\mathbf{q},s)\left[\frac{1}{\rho C_V(\mathbf{q})}-\frac{1}{\rho C_p(\mathbf{q})}\right],\qquad(2.31)$$

$$U_{12}(\mathbf{q},s)=U_{21}(\mathbf{q},s)=\frac{q^2\lambda(\mathbf{q},s)}{\rho}\times\left[\frac{1}{C_p(\mathbf{q})}\left(\frac{1}{C_V(\mathbf{q})}-\frac{1}{C_p(\mathbf{q})}\right)\right]^{1/2}.\qquad(2.32)$$

[20] See the article by R. Kubo in *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. I, Chap. 4.

The terms in U involving both vector currents and tensor currents like U_{23} are higher order in q and are probably negligible in describing the transport.

In summary, we list the significant terms in the matrix $(\delta_{ij}s-L_{ij}-U_{ij})$ in Table I. This matrix is almost diagonal. The last two rows and columns describe the diffusion of the transverse component of the momentum. The coupling term between the first row and column and the second is small and may be neglected. Then, the first row describes the heat-flow process, and the second and third rows describe the sound wave. When the sound-wave damping is small compared to its rate of oscillation, the sound waves obey a dispersion relation

$$s=\pm iq_x c(\mathbf{q})+\tfrac{1}{2}(q^2)D_s(\mathbf{q},s), \tag{2.33}$$

with

$$D_s(\mathbf{q},s)=\frac{\frac{4}{3}\eta(\mathbf{q},s)+\zeta(\mathbf{q},s)}{\rho}+\frac{\lambda(\mathbf{q},s)}{\rho}\left(\frac{1}{C_V(\mathbf{q})}-\frac{1}{C_p(\mathbf{q})}\right). \tag{2.34}$$

The eigenstates for these modes are

$$|\pm,\mathbf{q}\rangle=a_\pm(\mathbf{q})|\rangle=\frac{a_2(\mathbf{q})\pm a_3(\mathbf{q})}{\sqrt{2}}|\rangle. \tag{2.35}$$

We call the solution to Eq. (2.34)$s_\pm(q)$. Similarly, the heat-flow mode has a relaxation time which is a solution of

$$s=\lambda(\mathbf{q},s)q^2/\rho C_p(\mathbf{q}), \tag{2.36}$$

and we call this solution $s_T(\mathbf{q})$. Finally the viscous-flow mode has

$$s=\frac{\eta(\mathbf{q},s)q^2}{\rho}, \tag{2.37}$$

with a solution we call $s_\eta(\mathbf{q})$.

III. PERTURBATION THEORY FOR THE TRANSPORT COEFFICIENTS

A. Intermediate States

In the expressions (2.23), (2.28), and (2.29) for the transport coefficients, there appear structures of the form

$$X=1/(PLP-s), \tag{3.1}$$

which play the role of frequency denominators in the Kubo formula. To gain a convenient representation for X, we employ a representation of L in terms of its right eigenstates $|\nu,\mathbf{q}\rangle_R$, its left eigenstates ${}_L\langle\nu,\mathbf{q}|$, and its eigenvalues $s_\nu(\mathbf{q})$ by writing

$$L=\sum_{\nu'}\int\frac{d^3q'}{(2\pi)^3}|\nu',\mathbf{q}'\rangle_R s_{\nu'}(\mathbf{q}')_L\langle\nu',\mathbf{q}'|. \tag{3.2}$$

Here the eigenstates are normalized so that

$${}_L\langle\nu,\mathbf{q}|\nu',\mathbf{q}'\rangle_R=\delta_{\nu,\nu'}\delta(\mathbf{q}-\mathbf{q}')(2\pi)^3. \tag{3.3}$$

Because the projection operator P in X discriminates against local equilibrium states with wave vector $\mathbf{q}$, this projection operator almost entirely removes the lowest eigenstates of L (the transport states) and leaves the remaining states almost untouched. For this reason, we write the part of X with wave vector q as

$$X_\mathbf{q}=\sum_{\nu'=6}^{\infty}\frac{|\nu',\mathbf{q}\rangle_R\,{}_L\langle\nu',\mathbf{q}|}{s_{\nu'}(\mathbf{q})-s}. \tag{3.4}$$

We are interested in divergences in the transport coefficient $\eta(\mathbf{q},s)$ near the critical point. These divergences can be expected to arise from states ν' which give small values of $s_{\nu'}(q)$, that is slowly decaying intermediate states. There is one set of intermediate states which is particularly attractive for this consideration: those states involving multiple transport processes with long wavelengths. For example, we can consider a state which involves two independent transport processes with wave vectors $\mathbf{q}'$ and $\mathbf{q}-\mathbf{q}'$. These states would be of the structure

$$\sum_{\nu'}|\nu',\mathbf{q}\rangle_R\,{}_L\langle\nu',\mathbf{q}|=\tfrac{1}{2}\sum_{\nu_1=1}^{5}\sum_{\nu_2=1}^{5}\int\frac{d^3q'}{(2\pi)^3}\times a_{\nu_1}(\mathbf{q}')a_{\nu_2}(\mathbf{q}-\mathbf{q}')|\rangle\langle|a_{\nu_1}(-\mathbf{q})a_{\nu_1}(\mathbf{q}'-\mathbf{q}), \tag{3.5}$$

where the a_ν's are the linear combinations of the a_j's which generate specific transport processes. The eigenvalues for the states (3.5) are

$$s_{\nu'}(\mathbf{q})=s_{\nu_1}(\mathbf{q}')+s_{\nu_2}(\mathbf{q}'-\mathbf{q}), \tag{3.6}$$

since two noninteracting disturbances have an inverse relaxation time which is the sum of the inverse relaxation times for the individual disturbances.

With this logic, $X_\mathbf{q}$ gains a representation:

$$X_\mathbf{q}=\frac{1}{2!}\sum_{\nu\nu'}\int\frac{d^3q'}{(2\pi)^3}\frac{a_\nu(\mathbf{q}')a_{\nu'}(\mathbf{q}-\mathbf{q}')|\rangle\langle|a_\nu(-\mathbf{q}')a_{\nu'}(\mathbf{q}'-\mathbf{q})}{s_\nu(\mathbf{q}')+s_{\nu'}(\mathbf{q}-\mathbf{q}')-s}+\frac{1}{3!}\sum_{\nu\nu'\nu''}\int\frac{d^3q'}{(2\pi)^3}\frac{d^3q''}{(2\pi)^3}\times\frac{a_{\nu'}(\mathbf{q}')a_{\nu''}(\mathbf{q}'')a_\nu(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')|\rangle\langle|a_{\nu'}(-\mathbf{q}')a_{\nu''}(-\mathbf{q}'')a_\nu(\mathbf{q}'+\mathbf{q}''-\mathbf{q})}{s_\nu(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')+s_{\nu'}(\mathbf{q}')+s_{\nu''}(\mathbf{q}'')-s}+\cdots. \tag{3.7}$$

B. Viscous Flow → Heat Modes

To show the utility of the representation (3.7), we consider the formula for the viscosity

$$-q^2\eta(\mathbf{q},s)=\langle|g_y(-\mathbf{q})LPXPLg_y(\mathbf{q})|\rangle\beta. \quad (3.8)$$

In Eq. (3.8), the projection operators P may both be replaced by unity since $P-1$ makes no contribution to the matrix element. Consider the contributions to the right-hand side of (3.8) from intermediate states which involve two heat-flow modes. These give a contribution to $\eta(\mathbf{q},s)$ which is

$$-q^2\eta_{TT}(\mathbf{q},s)=\tfrac{1}{2}\beta\int\frac{d^3q'}{(2\pi)^3}\frac{\langle|g_y(-\mathbf{q})La_1(\mathbf{q}')a_1(\mathbf{q}-\mathbf{q}')|\rangle}{s_T(\mathbf{q}')+s_T(\mathbf{q}-\mathbf{q}')-s}\times\langle|a_1(\mathbf{q}'-\mathbf{q})a_1(-\mathbf{q}')Lg_y(\mathbf{q})|\rangle.$$

Since

$$\langle|a_1(-\mathbf{q}')a_1(\mathbf{q}'-\mathbf{q})Lg_y(\mathbf{q})|\rangle=-\langle|g_y(-\mathbf{q})La_1(\mathbf{q}')a_1(\mathbf{q}-\mathbf{q}')|\rangle^*,$$

this result may be rewritten as

$$q^2\eta_{TT}(\mathbf{q},s)=\frac{\beta}{2k_B^2}\int\frac{d^3q'}{(2\pi)^3}\times\frac{|M_{\mathbf{q},\mathbf{q}'}|^2}{[\rho C_p(\mathbf{q}')\rho C_p(\mathbf{q}-\mathbf{q}')][s_T(\mathbf{q}')+s_T(\mathbf{q}-\mathbf{q}')-s]}, \quad (3.9)$$

with

$$M_{\mathbf{q},\mathbf{q}'}=\langle|g_y(-\mathbf{q})Ls_{\mathrm{op}}(\mathbf{q}')s_{\mathrm{op}}(\mathbf{q}-\mathbf{q}')|\rangle. \quad (3.10)$$

To evaluate this matrix element, we successively commute L to the right and use $L|\rangle=0$ to write

$$M_{\mathbf{q},\mathbf{q}'}=\langle|g_y(-\mathbf{q})(-i\mathbf{q}')\cdot\mathbf{j}_{\mathrm{op}}{}^s(\mathbf{q}')s_{\mathrm{op}}(\mathbf{q}-\mathbf{q}')|\rangle+\langle|g_y(-\mathbf{q})[i(\mathbf{q}-\mathbf{q}')]\cdot\mathbf{j}_{\mathrm{op}}{}^s(\mathbf{q}-\mathbf{q}')s_{\mathrm{op}}(\mathbf{q}')|\rangle. \quad (3.11)$$

In this expression $\mathbf{j}^s$ is the heat-flow current which is

$$\mathbf{j}^s(\mathbf{r})=\left[\mathbf{j}^\epsilon(\mathbf{r})-\frac{\langle\epsilon+p\rangle}{\langle n\rangle}\mathbf{j}(r)\right]\Big/T. \quad (3.12)$$

This current has short-range correlations with the momentum density such that, when one averages over the momenta of all the particles, in the system, one finds

$$\beta\langle j_x{}^s(\mathbf{r})g_x(\mathbf{r}')\rangle_{\mathbf{q}}=\frac{1}{T}\delta(\mathbf{r}-\mathbf{r}')\left[\epsilon(\mathbf{r})+p(\mathbf{r})-\frac{\langle\epsilon+p\rangle}{\langle n\rangle}n(\mathbf{r})\right]=\delta(\mathbf{r}-\mathbf{r}')[s_{\mathrm{op}}(\mathbf{r})+p_{\mathrm{op}}(\mathbf{r})/T], \quad (3.13)$$

where p_{op} is the pressure operator. Thence, Eq. (3.11) reduces to

$$M_{\mathbf{q},\mathbf{q}'}=(-i\mathbf{q}_y')\beta^{-1}\langle|[s_{\mathrm{op}}(\mathbf{q}'-\mathbf{q})+(1/T)p_{\mathrm{op}}(\mathbf{q}'-\mathbf{q})]\times s_{\mathrm{op}}(\mathbf{q}-\mathbf{q}')|\rangle+i(\mathbf{q}_y'-\mathbf{q}_y)\beta^{-1}\times\langle|[s_{\mathrm{op}}(-\mathbf{q}')+(1/T)p_{\mathrm{op}}(-\mathbf{q}')]s_{\mathrm{op}}(\mathbf{q}')|\rangle. \quad (3.14)$$

The entropy operator s has been defined so that its correlations with the pressure vanishes, and so that its autocorrelations are related to $\rho C_p(\mathbf{q})$. Consequently,[21]

$$M_{\mathbf{q}\mathbf{q}'}=[i\mathbf{q}_y'C_p(\mathbf{q}-\mathbf{q}')+i(\mathbf{q}_y'-\mathbf{q}_y)C_p(\mathbf{q}')]\rho k_B{}^2T. \quad (3.15)$$

Since $q_y=0$, Eq. (3.9) reduces to

$$q^2\eta_{TT}(\mathbf{q},s)=\frac{1}{2\beta}\int\frac{d^3q'}{(2\pi)^3}(\mathbf{q}_y')^2\frac{[C_p(-\mathbf{q}+\mathbf{q}')-C_p(\mathbf{q}')]^2}{C_p(-\mathbf{q}'+\mathbf{q})C_p(\mathbf{q}')}\times\frac{1}{s_T(\mathbf{q}')+s_T(\mathbf{q}-\mathbf{q}')-s}. \quad (3.16)$$

In the static, long-wavelength limit $q\to 0$, $s\to 0$, Eq. (3.16) gives

$$\eta_{TT}(0,0)=\frac{1}{4}\int\frac{d^3q'}{(2\pi)^3}(q_y')^2\frac{\left[\frac{\partial}{\partial q_x'}C_p(\mathbf{q}')\right]^2}{s_T(\mathbf{q}')[C_p(\mathbf{q}')]^2}. \quad (3.17)$$

Because the thermal relaxation rate $s_T(\mathbf{q}')$ becomes very small for long wavelengths, this integral may contain large contributions from small values of q'. According to the scaling-law hypothesis, there is an inverse length, ξ^{-1}, which measures the characteristic wave vector for all phenomena near the critical point. From this hypothesis, one would conclude that main contributions to the q' integral come from $q'\lesssim\xi^{-1}$. Furthermore, in this region

$$\frac{\partial}{\partial q_x'}C_p(\mathbf{q}')\sim\frac{q_x'}{(q')^2}C_p(\mathbf{q}')$$

and

$$s_T(\mathbf{q}')|_{q'=\xi^{-1}}\sim s_T{}^*=(\lambda^*/\rho C_p)\xi^{-2}, \quad (3.18)$$

where $s_T{}^*$ stands for the inverse thermal relaxation time at $q'\sim\xi^{-1}$, and λ^* stands for the thermal conductivity at this wave vector and characteristic frequency. With these estimates in hand, we can estimate the right-hand side of Eq. (3.17) as

$$\eta_{TT}(\mathbf{q},s)\sim\frac{1}{\beta}\frac{\rho C_p}{\lambda^*}\xi^{-1} \quad (3.19)$$

for $q\lesssim\xi^{-1}$ and $s\lesssim s_T{}^*$.

Notice the restrictions on Eq. (3.19). For $q\gg\xi^{-1}$ or $s\gg s_T{}^*$, the frequency denominator in Eq. (3.16) is necessarily considerably increased. Therefore, if the restrictions in Eq. (3.19) are not satisfied, this contribution to $\eta(\mathbf{q},s)$ must necessarily be considerably reduced.

---

[21] Kawasaki evaluated matrix elements like (3.10) by a slightly different technique. He moved L to the left in (3.10) and obtained a matrix element with a factor of $q_x\tau_{xy}(-\mathbf{q})$, where τ_{xy} is the momentum current. He then argued that, at small q, $\tau_{xy}(\mathbf{q})$ reduced to $\beta^{-1}q_y'(\partial/\partial q_x')$. One can see that our result supports this conclusion.

Equation (3.19) is our first sight of a necessary divergence in a transport coefficient. If $\rho=\rho_c$ and $T>T_c$, according to the conventional notation C_p and ξ diverge as

$$C_p\sim\epsilon^{-\gamma},\quad \xi\sim\epsilon^{-\nu},$$

where $\epsilon=(T-T_c)/T_c$. Therefore, the product of the transport coefficients is

$$\eta_{TT}(\mathbf{0},0)\lambda^*\sim\epsilon^{-\gamma+\nu}. \tag{3.20}$$

Since γ is greater than ν, this result tends to indicate that one or both of the transport coefficients should diverge.

The same type of analysis may be employed to discuss the decay of a viscous mode into three or more heat modes. This analysis yields

$$q^2\eta_{TTT}(\mathbf{q},s)=\frac{\beta}{6k_BT}\int\frac{d^3q'}{(2\pi)^3}\frac{d^3q''}{(2\pi)^3}\times\frac{|M_{\mathbf{q},\mathbf{q}',\mathbf{q}''}|^2}{\rho^3C_p(\mathbf{q}')C_p(\mathbf{q}'')C_p(\mathbf{q}'+\mathbf{q}''-\mathbf{q})}\times\frac{1}{s_T(\mathbf{q}')+s_T(\mathbf{q}'')+s_T(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')-s}. \tag{3.21}$$

A typical term in M is

$$M_{\mathbf{q},\mathbf{q}',\mathbf{q}''}=\beta^{-1}q_xq_y'\frac{\partial}{\partial q_y'}\times\langle s_{\text{op}}(\mathbf{q}')s_{\text{op}}(\mathbf{q}'')s_{\text{op}}(-\mathbf{q}''-\mathbf{q}')\rangle. \tag{3.22}$$

We now employ the scaling idea to argue that the contribution (3.21) to η is of the same order of magnitude as the two heat-mode contribution, (3.9), which we have already evaluated. Consider how (3.21) differs from (3.9). There is an extra factor of C_p^{-1} in the denominator of (3.21) and an extra wave-number integral. If the wave-number integral contributes over $q''<\xi^{-1}$, this integral gives us an extra factor of ξ^{-3}. Finally, the matrix element (3.22) contains one more factor of $s_{\text{op}}(\mathbf{q}'')$ than (3.9). According to the scaling idea this extra factor enhances the matrix element by a factor of $|\epsilon|^{-\gamma-\beta}$ on the critical isochore. Of course, the frequency denominator is of the same order of magnitude, s_T^*, in both cases.

Hence the extra factors which appear in (3.21) and over and above the factors in Eq. (3.9) are $(\xi^{-3}/C_p)(\epsilon^{-\gamma-\beta})^2$ or $\epsilon^{3\nu-\gamma-2\beta}$. But according to the scaling idea, $3\nu=\gamma+2\beta$. (See Refs. 8 and 14.) Therefore, the contribution (3.21) is of the same order of magnitude as the contribution (3.9). An extension of the above argument indicates that all contributions from intermediate states with any number of heat modes in them are of the same order of magnitude.

C. Two Heat-Mode Contributions to $\zeta+\frac{4}{3}\eta$

The same kind of calculation works for $\zeta+\frac{4}{3}\eta$, with the only difference being that the predominant contributions come from the terms involving the local equilibrium part of the projection operator P.[22] In particular, the two heat-mode contribution to $\zeta+\frac{4}{3}\eta$ is

$$q^2[\zeta_{TT}(\mathbf{q},s)+\tfrac{4}{3}\eta_{TT}(\mathbf{q},s)]=\tfrac{1}{2}\beta\int\frac{d^3q'}{(2\pi)^3}\frac{|L_{\mathbf{q},\mathbf{q}'}|^2}{s_T(\mathbf{q}')+s_T(\mathbf{q}-\mathbf{q}')-s}. \tag{3.23}$$

Here

$$L_{\mathbf{q},\mathbf{q}'}=\langle|g_x(-\mathbf{q})LPa_1(\mathbf{q}')a_1(\mathbf{q}-\mathbf{q}')|\rangle\approx-\langle|g_x(-\mathbf{q})La_2(\mathbf{q})|\rangle\langle|a_2(-\mathbf{q})a_1(\mathbf{q}')a_1(\mathbf{q}-\mathbf{q}')|\rangle.$$

For small q and q' the matrix element is readily estimated as

$$L_{\mathbf{q},\mathbf{q}'}\sim-iqc\frac{(k_B)^{1/2}}{(\beta C_V)^{1/2}}T\left(\frac{\partial}{\partial T}\right)_{S/N}$$

so that the whole contribution to the viscosity is obtained by replacing the integrals in Eq. (3.23) in the same way as above. In this way we obtain

$$\zeta_{TT}(\mathbf{q},s)+\tfrac{4}{3}\eta_{TT}(\mathbf{q},s)\sim\frac{\rho C_p\xi^{-1}}{\lambda^*}\frac{k_Bc^2}{C_V}\left(\frac{T(\partial/\partial T)C_p|_{S/N}}{C_p}\right)^2 \tag{3.24}$$

for $q\lesssim\xi^{-1}$ and $s\lesssim s_T^*$. Or, if we use the scaling-law equality $3\nu=2-\alpha$ in the dimensional form

$$\xi^{-3}\left[\frac{1}{C_p}\frac{\partial C_p}{\partial T}\bigg|_{S/N}\right]^2\sim\beta^2k_B\rho C_V$$

on the critical isochore we have finally that

$$\zeta_{TT}(\mathbf{q},s)+\tfrac{4}{3}\eta_{TT}(\mathbf{q},s)\sim\frac{\rho^2c^2C_p\xi^2}{\lambda^*}$$

for $q\lesssim\xi^{-1}$ and $s\lesssim s_T^*$ on the critical isochore.

D. Heat $\rightarrow$ Heat + Viscous Flow

We use Eq. (2.29) to find $\lambda(\mathbf{q},s)$. The situation in which the intermediate state contains one heat-flow mode and one viscous-flow mode gives a contribution to $\lambda(\mathbf{q},s)$ which is

$$q^2\lambda_{\eta T}(\mathbf{q},s)=\frac{\beta}{k_B^2}\int\frac{d^3q'}{(2\pi)^3}\times\frac{|N_{\mathbf{q},\mathbf{q}'}|^2}{\rho^2C_p(\mathbf{q}')[s_T(\mathbf{q}')+s_\eta(\mathbf{q}-\mathbf{q}')-s]}. \tag{3.25}$$

[22] K. Kawasaki and M. Tanaka [Proc. Phys. Soc. (London) **90**, 791 (1967)] have calculated the contribution to $\zeta+\frac{4}{3}\eta$ from the local equilibrium part of the projection operator for a two-component liquid mixture.

TABLE II. Contributions to transport coefficients.

	Region I	Region II	Region III
	→Increasing s→	→	→
	$s\sim s^*_T\sim\frac{\lambda^*\xi^{-2}}{\rho C_p}\sim\epsilon^2$	$s\sim s^*_\eta\sim\frac{\eta^*\xi^{-2}}{\rho}\sim\epsilon^{4/3}$	$s\sim c\xi^{-1}\sim\epsilon^{2/3}$
Contributions to λ:			
From viscous flow plus heat modes	$\lambda\sim\frac{\rho C_p\xi^{-1}}{\beta\eta^*}\sim\epsilon^{-2/3}$ →	→	
From sound waves plus heat modes	$\lambda\sim\frac{\xi^{-2}C_p}{c\beta}\sim\epsilon^0$ →	→	→
Contributions to η:			
From heat modes	$\eta\sim\frac{\rho C_p\xi^{-1}}{\beta\lambda^*}\sim\epsilon^0$		
From sound waves plus heat modes	→	$\eta\sim\frac{C_p\xi^{-2}}{c\beta C_V}\sim\epsilon^0$ →	→
Contributions to ζ:			
From heat modes	$\zeta\sim\frac{\rho^2c^2C_p\xi^2}{\lambda^*}\sim\epsilon^{-2}$		
From sound waves plus heat modes	→	$\zeta\sim\rho c\xi\sim\epsilon^{-\nu+\alpha/2}\sim\epsilon^{-2/3}$ →	→
From high q processes	→	$\eta\sim\zeta\sim\lambda\sim$constant →	→

If the direction of the momentum in the intermediate state is described by the unit vector $\hat{n}$, then

$$N_{\mathbf{q},\mathbf{q}'}=\langle|s_{\mathrm{op}}(-\mathbf{q})LP\hat{n}\cdot\mathbf{g}(\mathbf{q}-\mathbf{q}')s_{\mathrm{op}}(\mathbf{q}')|\rangle.$$

In the thermal conductivity matrix elements, the contribution of $(P-1)$ is once again negligible. Consequently,

$$\begin{aligned}N_{\mathbf{q},\mathbf{q}'}&=i\mathbf{q}\cdot\langle|\,\mathbf{j}_{\mathrm{op}}{}^{s}(-\mathbf{q})\hat{n}\cdot\mathbf{g}(\mathbf{q}-\mathbf{q}')s_{\mathrm{op}}(\mathbf{q}')|\rangle\\&=i\mathbf{q}\cdot\hat{n}\beta^{-1}\langle|[s_{\mathrm{op}}(-\mathbf{q}')+p_{\mathrm{op}}(-\mathbf{q}')/T]s_{\mathrm{op}}(\mathbf{q}')|\rangle\\&=i\mathbf{q}\cdot\hat{n}\beta^{-1}k_B\rho C_p(\mathbf{q}').\end{aligned}$$

After averaging over directions of $\mathbf{q}'$ and summing over polarization vectors, $\hat{n}$, perpendicular to $\mathbf{q}-\mathbf{q}'$, we find

$$\lambda_{\eta T}(q,s)=\tfrac{1}{3}\beta^{-1}\int\frac{d^3q'}{(2\pi)^3}\frac{C_p(\mathbf{q}')}{s_T(\mathbf{q}')+s_\eta(\mathbf{q}-\mathbf{q}')-s}.\quad(3.26)$$

The factor $C_p(\mathbf{q}')$ in the numerator of Eq. (3.26) allows this contribution to λ to be large. The integral contributes for $q'\lesssim\xi^{-1}$. Since the thermal diffusion rate is very slow near the critical point, the viscous relaxation rate $s_\eta(\mathbf{q}')$ dominates the thermal relaxation rate in the denominator. As a result

$$\lambda_{\eta T}(\mathbf{q},s)\sim\frac{\rho C_p\xi^{-1}}{\eta^*\beta},\quad\text{for}\quad q\lesssim\xi^{-1},\quad s\lesssim s_\eta^*.\quad(3.27)$$

Here s_η^* is the viscous relaxation rate at the wave number ξ^{-1}, i.e.,

$$s_\eta(q')|_{q'=\xi^{-1}}\sim s_\eta^*=(\eta^*/\rho)\xi^{-2}.\quad(3.28)$$

The limitations on Eq. (3.27) indicate that for large s and large q the denominator in Eq. (3.26) becomes large enough to reduce the size of the contribution to the thermal conductivity quite appreciably.

From scaling-law arguments we conclude that contributions with two or more heat-flow modes in the intermediate state together with a viscous-flow mode give a contribution to λ of the same order as (3.27).

If there are no further contributions to η and λ, we would now have enough information to compute both η and λ. To do this calculation, it is necessary to recognize that the large factor C_p in the denominator of s_T guarantees that, as indicated in Table II, $s_T^*\ll s_\eta^*$.

Therefore, η^* is the viscosity evaluated at "frequencies" much higher than s_T^*. The contributions (3.19) to η cut off at the characteristic thermal relaxation rate s_T. Hence, η^* gains nothing from the processes involving heat-flow modes in intermediate states.

If these be the only processes contributing to the analomous viscosity, there cannot be any critical fluctuation term in η^*. Then η^* will be finite at the critical point and Eq. (3.27) will predict

$$\lambda(\mathbf{0},0)\sim\epsilon^{-\gamma+\nu}, \qquad (3.29)$$

which diverges as roughly the $-\frac{2}{3}$ power of $T-T_c$ on the critical isochore. Furthermore, the contribution (3.29) will persist for all $s\lesssim s_\eta^*$. Hence, it will be quite relevant up to and beyond the thermal cut off s_T^*. This means that we can use (3.29) to evaluate λ^* in Eq. (3.19). We then find

$$\eta_{TT}(\mathbf{q},s)\sim\epsilon^0, \quad \text{for} \quad q<\xi^{-1} \quad \text{and} \quad s<s_T^*. \qquad (3.30)$$

Since η^* is, by our hypothesis of leaving out other contributions, quite finite, Eq. (3.30) predicts $\eta_{TT}(\mathbf{0},0)$ does not diverge as a power of $T-T_c$. This result does not preclude a logarithmic behavior[23] or a very strong cusp in the low-frequency viscosity. In fact, this analysis suggests that one of these two types of singularities might well hold for η.

Our conclusions about the low-frequency behavior of λ and η will depend quite crucially upon the high-frequency form of η. High-frequency processes which can contribute to η include those in which sound waves are produced. The characteristic frequency for sound waves is $c\xi^{-1}$, which is much higher than s_η^* or s_T^*. Therefore, as indicated sound-wave processes are good candidates for producing contributions to λ, η, and ζ, which will not cut off until high frequencies.

E. Sound-Wave Intermediate States for λ

Intermediate states with two sound waves do not produce an appreciable contribution to $\lambda(\mathbf{q},s)$. However, three-sound-wave intermediate states do produce a contribution, which can be computed from

$$q^2\lambda_{ppp}(\mathbf{q},s)=\frac{1}{3!k_B}\int\frac{d^3q'}{(2\pi)^3}\frac{d^3q''}{(2\pi)^3}\sum_{\sigma,\sigma',\sigma''=\pm1}\frac{|\langle|\mathbf{q}\cdot\mathbf{j}_{\text{op}}{}^s(-\mathbf{q})a_{\sigma'}(\mathbf{q}')a_{\sigma''}(\mathbf{q}'')a_\sigma(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')|\rangle|^2}{s_{\sigma'}(\mathbf{q}')+s_{\sigma'}(\mathbf{q}'')+s_\sigma(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')-s}, \qquad (3.31)$$

with

$$a_{\sigma'}(\mathbf{q})=\frac{1}{\sqrt{2}}\left[a_2(\mathbf{q})+\sigma'\frac{\mathbf{q}\cdot\mathbf{g}(\mathbf{q})}{|\mathbf{q}|}\left(\frac{\beta}{\rho}\right)^{1/2}\right], \qquad (3.32)$$

$$s_{\sigma'}(\mathbf{q})=\sigma'ic(\mathbf{q})|\mathbf{q}|+\tfrac{1}{2}D_s(\mathbf{q},s_{\sigma'}(\mathbf{q}))q^2. \qquad (3.33)$$

The significant terms in the product of three a's are the ones which involve a product of two a_2's with one momentum. After the momentum average is performed, we find that the matrix element in Eq. (3.31) is

$$\frac{1}{\sqrt{(\rho\beta)}}\frac{1}{(\sqrt{2})^3}\langle|\left\{\frac{\mathbf{q}\cdot\mathbf{q}'}{|\mathbf{q}'|}\sigma'[s_{\text{op}}(-\mathbf{q}+\mathbf{q}')+p_{\text{op}}(-\mathbf{q}+\mathbf{q}')/T]a_2(\mathbf{q}'')a_2(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')\right.$$
$$+\frac{\mathbf{q}\cdot\mathbf{q}''}{|\mathbf{q}''|}\sigma''[s_{\text{op}}(-\mathbf{q}+\mathbf{q}'')+p_{\text{op}}(-\mathbf{q}+\mathbf{q}'')/T]a_2(\mathbf{q}')a_2(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')$$
$$\left.+\frac{\mathbf{q}\cdot(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')}{|\mathbf{q}-\mathbf{q}'-\mathbf{q}''|}\sigma[s_{\text{op}}(-\mathbf{q}'-\mathbf{q}'')+p_{\text{op}}(-\mathbf{q}'-\mathbf{q}'')/T]a_2(\mathbf{q}')a_2(\mathbf{q}'')\right\}|\rangle.$$

If q, q', and q'' are each $\lesssim\xi^{-1}$, this matrix element may be estimated to be of the order of

$$\frac{1}{\sqrt{(\rho\beta^3)}}q\frac{1}{C_V}\left(\frac{\partial}{\partial T}C_V\right)_p,$$

since $s_{\text{op}}(-q)$ generates $\beta^{-1}(\partial/\partial T)$ as $q\to0$ and $\langle|a_2(-\mathbf{q})a_2(\mathbf{q})|\rangle$ is of order unity.

The damping terms, i.e., the real part, of the frequency denominator of Eq. (3.31) are smaller or of the same order as the imaginary part of this denominator. Therefore, to get an order of magnitude estimate we can replace the denominator by the δ function

$$\delta(\sigma c(\mathbf{q}')q'+\sigma''c(\mathbf{q}'')q''+\sigma c(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')|\mathbf{q}-\mathbf{q}'-\mathbf{q}''|-\text{Im}s),$$

which generates a contribution

$$\sim\frac{1}{c\xi^{-1}}, \quad \text{for} \quad |s|\lesssim c\xi^{-1}.$$

Since each q intergral covers $q\lesssim\xi^{-1}$, the resulting estimate of λ is

$$\lambda_{ppp}(\mathbf{q},s)\sim\frac{\xi^{-5}}{c}\frac{1}{C_V^2}\left[\left(\frac{\partial C_V}{\partial T}\right)_p\right]^2\frac{1}{\rho\beta^3k_B}. \qquad (3.34)$$

The scaling-law arguments inform us that the two $(\partial/\partial T)_p$ each produce a factor $\epsilon^{-\beta-\gamma}$ multiplying the

[23] The scaling-law analysis is based upon exponents and it cannot distinguish a finite but discontinuous result from a logarithmic infinity.

singular part of C_V while $\xi^{-3}\sim\epsilon^{3\nu}=\epsilon^{2\beta+\gamma}$. If we put this argument in dimensional form, we find that

$$\beta^{-2}\xi^{-3}(\partial/\partial T)_p{}^2\sim k_B C_p\rho$$

so that Eq. (3.34) can be written

$$\lambda_{ppp}(\mathbf{q},s)\sim\frac{\xi^{-2}}{c}\frac{C_p}{C_V{}^2}\frac{1}{\beta}\{[C_V]_{\text{sing}}\}^2,$$

$$\text{for}\quad q\lesssim\xi^{-1},\quad |s|\lesssim c\xi^{-1}. \tag{3.35}$$

Here the subscript "sing" reminds us to take the singular part of C_V in our estimates and leave out any constant term which might appear. If C_V diverges as $\epsilon^{-\alpha}$ Eq. (3.35) gives an estimate of a singular contribution to λ, which is

$$\lambda_{ppp}(0,0)\sim\epsilon^{-\gamma+2\nu-\alpha/2} \tag{3.36}$$

on the critical isochore. Since $\gamma-2\nu\approx0$, Eq. (3.36) describes a weakly divergent or strongly cusped contribution to the high-frequency sound-wave damping constant.

If the intermediate state includes in addition to sound waves viscous flow and heat modes, the scaling-law arguments imply that the estimate (3.35) still gives the correct order of magnitude for the singular parts of $\lambda(\mathbf{q},s)$ at high frequencies.

F. Sound-Wave Intermediate States for η

The contribution to η from a three-sound-wave intermediate state is given by

$$q^2\eta_{ppp}(q,s)\sim\beta\int d^3q'd^3q''|M_{\mathbf{q},\mathbf{q}',\mathbf{q}''}|^2$$
$$\times\sum_{\sigma\sigma'\sigma''=\pm1}\frac{1}{s_{\sigma'}(\mathbf{q}')+s_{\sigma''}(\mathbf{q}'')+s_\sigma(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')-s}, \tag{3.37}$$

where a typical term in M is

$$M_{\mathbf{q},\mathbf{q}',\mathbf{q}''}=\langle|g_y(-\mathbf{q})[L,a_2(\mathbf{q}')]$$
$$\times a_2(\mathbf{q}'')a_2(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')|\rangle. \tag{3.38}$$

Equation (2.15b) implies that

$$[L,a_2(\mathbf{q}')]=\frac{(\rho\beta)^{1/2}}{\langle n\rangle}c(\mathbf{q}')(-i\mathbf{q}')\cdot\mathbf{j}_{\text{op}}(\mathbf{q}')$$
$$+\left\{\frac{1}{k_B\rho}\left[\frac{1}{C_V(\mathbf{q}')}-\frac{1}{C_p(\mathbf{q}')}\right]\right\}^{1/2}(-i\mathbf{q}')\cdot\mathbf{j}_{\text{op}}{}^s(\mathbf{q}'),$$

so that a momentum average gives

$$\beta\langle g_y(-\mathbf{q})[L,a_2(\mathbf{q}')]\rangle_{\mathbf{q}}=\frac{(\rho\beta)^{1/2}}{\langle n\rangle}c(\mathbf{q}')(-iq_y')n_{\text{op}}(\mathbf{q}'-\mathbf{q})$$
$$+\left\{\frac{1}{k_B\rho}\left[\frac{1}{C_V(\mathbf{q}')}-\frac{1}{C_p(\mathbf{q}')}\right]\right\}^{1/2}(-iq_y')$$
$$\times\left[s_{\text{op}}(\mathbf{q}'-\mathbf{q})+\frac{p_{\text{op}}(\mathbf{q}'-\mathbf{q})}{T}\right]. \tag{3.39}$$

At this point, a serious question arises. What is the behavior of the collection of operators in Eq. (3.39) for $q\sim\xi^{-1}$, $q'\sim\xi^{-1}$? At $q=0$, the answer is clear. Since p_{op} has only weak fluctuations and may be neglected, expression (3.39) is $-iq_y'a_2(q')$ at $q=0$. But for $q\neq0$ each of the two terms on the right-hand side of (3.39) is of order $c(\mathbf{q}')a_1(\mathbf{q}'-\mathbf{q})$, which is much more singular than $a_2(\mathbf{q}'-\mathbf{q})$. The question then boils down to: Do the most singular parts of the two terms in Eq. (3.39) cancel against one another?

There is an alternative way of stating this problem. If the product $[C_V(\mathbf{q}')]^{1/2}c(\mathbf{q}')$ is independent of q', then (3.39) is proportional to $a_2(\mathbf{q}'-\mathbf{q})$. If, however,

$$\frac{\partial}{\partial q'}[C_V(\mathbf{q}')]^{1/2}c(\mathbf{q}')\sim\xi, \tag{3.40}$$

then expression (3.39) is of the order of $q'ca_1(\mathbf{q}')$. This idea was discussed at the end of Sec. IIC. We stated there the point that the product $[C_V(\mathbf{q}')]^{1/2}c(\mathbf{q}')$ would be essentially independent of $q'\xi$ if the strongest way of stating the scaling-law idea were right. However, we believe this to be probably an overextension of the scaling-law idea. In any case, we here use the estimate (3.40) and concomitant estimate of the matrix element defined in Eq. (3.38) as

$$M_{\mathbf{q},\mathbf{q}'\mathbf{q}''}\sim\frac{q}{\beta}\left(\frac{1}{k_B\rho C_V}\right)^{1/2}$$
$$\times\langle|s_{\text{op}}(\mathbf{q}'-\mathbf{q})a_2(\mathbf{q}'')a_2(\mathbf{q}-\mathbf{q}'-\mathbf{q}'')|\rangle.$$

From this point on we can use the same analysis as for λ_{ppp}, and we find

$$\eta_{ppp}(\mathbf{q},s)\sim\lambda_{ppp}(\mathbf{q},s)/C_V. \tag{3.41}$$

G. Sound-Wave Intermediate States for $\zeta+\frac{4}{3}\eta$

Two-sound-wave processes contribute a term to the longitudinal viscosity

$$q^2[\zeta_{pp}(\mathbf{q},s)+\tfrac{4}{3}\eta_{pp}(\mathbf{q},s)]$$
$$=\tfrac{1}{2}\beta\sum_{\sigma,\sigma'=\pm1}\int\frac{dq'}{(2\pi)^3}\frac{|H_{\mathbf{q},\mathbf{q}'}|^2}{s\sigma(q')+s\sigma'(q-q')-s},$$

with

$$H_{\mathbf{q},\mathbf{q}'}=\langle|g_x(-\mathbf{q})LPa_2(\mathbf{q}')a_2(\mathbf{q}-\mathbf{q}')|\rangle \approx -\langle|g_x(-\mathbf{q})La_2(\mathbf{q})|\rangle \times\langle|a_2(-\mathbf{q})a_2(\mathbf{q}')a_2(\mathbf{q}-\mathbf{q}')|\rangle. \quad (3.42)$$

For small q and q', H reduces to

$$H_{\mathbf{q},\mathbf{q}'}\sim -iq\frac{(k_B)^{1/2}}{(\beta C_V)^{1/2}}T\frac{\partial}{\partial T}c|_{S/N}, \quad (3.43)$$

so that the contribution to $\zeta+\frac{4}{3}\eta$ may be estimated as

$$\zeta_{pp}(\mathbf{q},s)+\tfrac{4}{3}\eta_{pp}(\mathbf{q},s)\sim\frac{1}{C_Vc}\xi^{-2}k_B\left[T\frac{\partial c}{\partial T}\bigg|_{S/N}\right]^2 \quad (3.44)$$

for $q\lesssim\xi$, $|s|\lesssim c\xi^{-1}$. Or if we use the scaling-law result $3\nu=2-\alpha$ in the dimensional form

$$\xi^{-3}\left[\frac{1}{c}\frac{\partial c}{\partial T}\bigg|_{S/N}\right]^2\sim\beta^2k_B\rho C_V$$

on the critical isochore we find

$$\zeta_{pp}(\mathbf{q},\mathbf{s})\sim\rho c\xi$$

on the critical isochore.

IV. SUMMARY

In this section we summarize our results. (See Table II.) Note that the rough temperature dependences of quantities are also given in Table II taking ξ to diverge roughly as the $-\frac{2}{3}$ power of ϵ, C_p to diverge roughly as the $-\frac{4}{3}$ power of ϵ, and C_V to be roughly logarithmically divergent.

There are basically three different frequency regions: the low-frequency domain

$$s\lesssim s_T^*=(\lambda/\rho C_p)\xi^{-2}, \quad \text{(region I)} \quad (4.1a)$$

the intermediate region

$$s_T\ll s\lesssim s_\eta^*=\eta^*\xi^{-2}/\rho, \quad \text{(region II)} \quad (4.1b)$$

and the high-frequency region

$$s_\eta^*\ll s\lesssim c\xi^{-1}. \quad \text{(region III)} \quad (4.1c)$$

To state our results, we start from the high-frequency region and work down. In all our statements we assume $q\lesssim\xi^{-1}$.

In region III, $\lambda(q)$ has a singular part given by Eq. (3.35). If C_V is divergent at the critical point, this singular part of λ is given by

$$\lambda\sim\frac{\xi^{-2}}{c}\frac{C_p}{\beta}. \quad \text{(region III)} \quad (4.2a)$$

On the critical isochore, this gives

$$\lambda\sim\epsilon^{2\nu-\gamma-\alpha/2}. \quad (4.2b)$$

The exponent here probably lies within one- or two-tenths of zero. In addition to this strong cusp or weak infinity, there is also a constant term in λ coming from high wave numbers. In this region there are probably also weakly divergent or strongly cusped terms in η which we estimate as

$$\eta\sim\frac{\xi^{-2}}{c\beta}\frac{C_p}{C_V}, \quad \text{(region III and region II)} \quad (4.3a)$$

which behave like

$$\eta\sim\epsilon^{2\nu-\gamma+\alpha/2} \quad (4.3b)$$

on the critical isochore. On the other hand, ζ is much more strongly infinite than η. From Eq. (3.44)

$$\zeta\sim\frac{\xi^{-2}}{cC_V}k_B\left[T\frac{\partial c}{\partial T}\bigg|_{S/N}\right]^2 \quad \text{(region III and region II)} \quad (4.4a)$$
$$\sim\xi c\rho,$$

so that on the critical isochore

$$\zeta\sim\epsilon^{2\nu-2+\alpha/2}, \quad (4.4b)$$

which is roughly a $(-\frac{2}{3})$-power divergence.

The terms in Eq. (4.3) also seem to be the most important singular terms in η in region II. If these terms go to infinity, they dominate the behavior of η so that Eq. (3.27) gives

$$\lambda\sim\rho C_Vc\xi, \quad (4.5a)$$

and on the critical isochore we have

$$\lambda\sim\epsilon^{-\alpha/2-\nu}, \quad (4.5b)$$

if C_V diverges as $\epsilon^{-\alpha/2}$. Since α is small and $\nu\approx0.6$, this result indicates a rather strong divergence in the thermal conductivity. If, on the other hand, the singularities in Eq. (4.3) lead to a cusp rather than an infinity in η, then the constant term in η will dominate near the critical point. If we call this constant η_∞, we have from Eq. (3.27)

$$\lambda\sim\frac{\rho C_p\xi^{-1}}{\beta\eta_\infty} \quad \text{(regions I and II)} \quad (4.6a)$$

and on the critical isochore

$$\lambda\sim\epsilon^{-\gamma+\nu}, \quad (4.6b)$$

which is again roughly a $\frac{2}{3}$ power-law divergence. If the scaling laws were so fully correct as to prevent the high-frequency singularities in η, then Eqs. (4.6) would be correct rather than Eqs. (4.5).

Whatever form the singularities in λ might take, our approach predicts that λ will vary smoothly as one goes from region II into region I. That is to say that both the coefficient in front of the singularity and the critical exponent will remain constant as s passes through s_T^*. However, as one passes into region I, new processes become possible which make for new contributions to η. If η turns out to be divergent in region II, our approach predicts that it will have the same critical exponent in region I, but the coefficient preceding the divergent term might well increase markedly as one passed into region I. If η turns out to be nondivergent in region II, the integrals which defines it appears to diverge as ϵ^0 in region I. This should be read to mean that η can diverge logarithmically in region I if there is no divergence in regions II and III. On the other hand, ζ has a very strong divergence in region I. According to Eq. (3.24)

$$\zeta \sim \frac{\rho C_p \xi^{-1}}{\lambda^*} \frac{k_B c^2}{C_V} \left[\frac{T(\partial C_p/\partial T)_{S/N}}{C_p} \right]^2$$

$$\sim (C_p/C_V)\xi c \rho, \quad \text{(region I)} \tag{4.7a}$$

so that on the critical isochore

$$\zeta \sim \epsilon^{-\gamma-\nu+(3/2)\alpha}, \tag{4.7b}$$

which diverges roughly as ϵ^{-2}.

Finally, we notice one characteristic feature of the sound-wave damping constant:

$$D_s = \frac{\lambda}{\rho C_V} + \frac{\zeta + \frac{4}{3}\eta}{\rho}.$$

According to Eqs. (4.5) and (4.4), in regions II and III

$$D_s = A \xi c, \tag{4.8}$$

where A is a constant of order unity. Then in this region the sound-wave dispersion relation will read

$$s = \pm icq + \tfrac{1}{2} A c (q\xi) q$$

or

$$s = cq[\pm i + \tfrac{1}{2} A q \xi]. \tag{4.9}$$

Notice the dependence of this expression upon the characteristic parameter $q\xi$. Several recent authors[24,25] have used the assumption that frequencies of modes near the critical point depend upon $q\xi$ to relate apparently different transport phenomena near the critical point. In particular, they have estimated the order of magnitude of damping terms by assuming that the complex frequency of the oscillations were functions of the form

$$s = q^x f(q\xi). \tag{4.10}$$

Equation (4.9) is precisely of the form of (4.10). Hence, our arguments have provided one case in which this scaling assumption about frequencies can be derived from microscopic considerations. Notice, however, that in our case Eq. (4.4) only holds for the relatively high frequencies of regions II and III. However, in region I, ζ is considerably enhanced in size. Hence, in this region, the assumptions of Ferrel *et al.*,[24] and Halperin and Hohenberg[25] do not serve to predict the sound-wave damping constant.

The divergence of λ predicted by this work seems to agree with the experimental results of Cummins and Swinney[26] for CO_2, while it disagrees, for $T > T_c$, with the experiment of Ford and Benedek[27] on SF_6.

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