

Transport Coefficients Near the Consolute Temperature of a Binary Liquid Mixture*

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Transport coefficients are computed near the critical mixing point of a classical binary liquid mixture by considering processes in which one transport mode breaks up into several. The conclusions are that, when the concentration has its critical value and the temperature is near the consolute temperature, the diffusion coefficient does not go to zero as fast as $(\partial\mu_{12}/\partial x)_{P,T}$, but only as fast as $\xi^{-1} \approx |T-T_c|^{2/3}$, where ξ is the temperature-dependent coherence length; that the shear viscosity has at most a logarithmic divergence; that the thermal diffusion coefficient has at most a very weak divergence; and that the thermal conductivity has no divergent part. A result very similar to that of Kawasaki and Tanaka is found for the bulk viscosity.

I. INTRODUCTION

In several recent papers, correlation function or equivalent response function techniques¹⁻⁹ have been applied to the problem of calculating the apparent divergences¹⁰ in transport coefficients near critical points. In particular, these methods have been used to predict the apparent singular behavior of the shear viscosity^{1,2,5,8} and bulk viscosity or sound-wave damping constant^{3,7,8} of a binary liquid mixture near its critical mixing point.

In this paper the perturbation formalism for transport coefficients of Ref. 9 and the "scaling laws"¹¹⁻¹³ for static correlation functions are used to discuss this same problem. The basic difference between our work and that of the above authors¹⁻⁸ is this use of the scaling laws rather than the Ornstein-Zernike theory to estimate correlation functions. The scaling laws probably yield more accurate estimates very close to the critical point.

The next section of the paper is devoted to an analysis of the diffusion coefficient and shear viscosity based upon the work of Ref. 9. The final section explains how a more detailed theory leads to the same results for D and η , and to additional information which the simpler analysis of Sec. III does not yield.

II. CONNECTION BETWEEN BINARY MIXTURE AND LIQUID-GAS CASE

The calculation of transport coefficients for the case of a binary liquid mixture is very similar to that for the case of a liquid gas. The basic difference is that there is one extra variable and thus one more transport mode in the mixture than in the liquid-gas problem.

The thermal conductivity of a mixture is, from experiment,¹⁰ apparently nonsingular near the consolute temperature. This suggests that the thermal conduction mode is irrelevant for our purposes, and provides the basis for the calculation of this section, since the calculation of transport coefficients for the mixture is essentially the same as that for the liquid-gas case if the extra transport mode may be neglected.

In this section of the paper we assume that the

thermal conduction mode is irrelevant. Then we can obtain the anomalous contributions to the bulk viscosity η and diffusion coefficient¹⁴ D of a mixture near its consolute temperature by simply identifying the appropriate variables with those of a one-component gas and using the results of Ref. 9 for the anomalous transport coefficients near the liquid-gas critical point.

A. Connections Among Thermodynamic Variables

The basic connection to be made among the thermodynamic variables of the two problems is that between the order parameters.^{15,16} Thus the order parameter in the phase separation problem, the concentration of one component of the mixture minus its critical value^{16,17} is to be identified with the order parameter in the liquid-gas case, the density minus the critical density.

A more complete list of identifications is given in Table I. In addition to the connection between the order parameters, there are also connections between their respective conjugate thermodynamic variables as well as their derivatives with respect to these variables. The relation between the specific heat at constant pressure for the mixture and the constant-volume heat capacity for the gas has been given by Rowlinson.¹⁸

There is one extra intensive variable, the pressure, in the mixture case. However, for our purposes the pressure is irrelevant and thus does not affect the correspondences.

The identification of variables given in Table I is not perfect because β , the "critical exponent" which describes how the jump in the order parameter goes to zero near the second-order phase transition,^{16,17} is different for the two cases. For the mixture,¹⁹ $\beta \approx 0.31$; while for the liquid-gas system,¹⁶ $\beta \approx 0.34-0.35$.

B. Connections Among Transport Processes

To make further progress we have to give the connections among transport processes. The basic correspondence to be made is that between modes in which the order parameters enter.

When the temperature is near the consolute temperature, the two diffusive solutions of the

TABLE I. The variable in the mixture problem is to be identified with indicated variable in the liquid-gas problem. The subscripts (1) and (2) refer to the two different species comprising the mixture, and m denotes the mass of the particles.

Binary mixture	Liquid gas
x (concentration)	ρ (density)
$\mu_{12} = (\mu_1/m_1) - (\mu_2/m_2)$	μ (chemical potential)
$(\partial x / \partial \mu_{12}) _{P, T}$	$(\partial \rho / \partial \mu) _T$
T	T (temperature)
C_P	C_V

hydrodynamic equations describing the mixture can be approximately broken up into a mode dominated by mass diffusion and another by thermal conduction.²⁰ The mass diffusion mode is of course the mode into which the order parameter enters.

In the liquid-gas case the thermal conduction mode is the mode into which the variable with the large critical fluctuations enters. This is so because the entropy contains the large fluctuations of the density; i. e., C_P and $(\partial \rho / \partial \mu)_T$ diverge in the same manner near the critical point. Thus we identify the mass diffusion mode in the mixture problem with the thermal conduction mode in the liquid-gas problem. The full list of correspondences is given in Table II. The thermal diffusivity $\lambda / \rho C_P$, rather than the thermal conductivity λ , has been identified with D , since it is this quantity which determines how fast the thermal mode relaxes.

The characteristic frequencies s_D^* , s_η^* , and s_T^* are defined as in Ref. 9. That is, s_D^* is the inverse diffusion relaxation time evaluated at wave number $q \sim \xi^{-1}$ and D^* is the diffusion coefficient evaluated at this wave number and frequency. Similar definitions hold for s_η^* and η^* and s_T^* and λ^* . All these frequencies go to zero strongly near the consolute temperature. In Table II, ξ denotes the temperature-dependent coherence length.¹⁶ When the concentration has its critical value and the temperature is near the consolute temperature, ξ diverges as $|T - T_c|^{-\nu}$, where²¹ probably $\nu \approx \frac{2}{3}$.

For the purposes of this section, the thermal

TABLE II. Identification of transport modes in the mixture problem with the corresponding modes in the liquid-gas problem.

Binary liquid mixture	Liquid gas
Mass diffusion mode D	Heat conduction mode $(\lambda / \rho C_P)$
$s_D^* \sim D^* \xi^{-2}$	$s_T^* \sim \lambda^* \xi^{-2} / \rho C_P$
Viscous flow η	Viscous flow η
$s_\eta^* \sim \eta^* \xi^{-2} / \rho$	$s_\eta^* \sim \eta^* \xi^{-2} / \rho$
Thermal conduction } sound waves }	Sound waves

conduction mode and sound-wave modes of the mixture are identified with the sound-wave modes of the liquid-gas system. In Ref. 9 it was found that the sound-wave modes made no contribution to the low-frequency transport coefficients under the assumption that the strongest form of the scaling laws held. We are assuming here that the heat-conduction mode and sound waves are irrelevant, so that we can write down the singular parts of the low-frequency transport coefficients by referring to Ref. 9 and the identifications in Table II.

The singular part of the shear viscosity is given in Eq. (3.30) of Ref. 9 for the liquid-gas case. This then implies that the wave vector and frequency-dependent shear viscosity of the mixture is given by

$$\eta(\vec{q}, s) \sim |T - T_c|^0 \quad (1)$$

for $q \lesssim \xi^{-1}$ and $s \lesssim s_D^*$ when the concentration has its critical value. In Eq. (1), s is the imaginary frequency (Laplace transform variable) describing the disturbance. Equation (1) implies that η does not diverge as a power of $T - T_c$ near the consolute temperature, but has at most a logarithmic divergence or strong cusp.

The singular contribution to the zero wave vector and frequency thermal conductivity for the liquid-gas case is given by Eq. (3.29) in Ref. 9, which is

$$\lambda(\vec{0}, 0) / |T - T_c|^{-\gamma} \sim |T - T_c|^\nu \quad (\text{liquid-gas}).$$

The left-hand side of the above equation is proportional to $\lambda / \rho C_P$, since C_P diverges as $|T - T_c|^{-\gamma}$. From our list of correspondences this then implies that

$$D(\vec{0}, 0) \sim |T - T_c|^\nu \sim \xi^{-1} \quad (2)$$

for the concentration having its critical value.

Like the thermal diffusivity, D may be written as a transport coefficient L divided by a thermodynamic derivative $(\partial x / \partial \mu_{12})_{P, T}$.²² Then, since near the consolute temperature $(\partial x / \partial \mu_{12})_{P, T} \sim |T - T_c|^{-\gamma}$ with γ greater than or about unity,²³ Eq. (2) implies that the transport coefficient L diverges as $|T - T_c|^{\nu - \gamma}$. Since $\nu \approx \frac{2}{3}$, the behavior of D described by (2) seems to be in rough agreement with the experiment of Chu, Schonnes, and Kao²² who studied the mixture isobutyric acid water and also with the experiment of Chen and Polonsky²⁴ on the mixture n -hexane-nitrobenzene.

III. MORE DETAILED THEORY

The results (1) and (2) are based upon the assumption that no appreciable contribution to the anomalous parts of the transport coefficients comes from the heat-conduction mode. In this section, the results of a more detailed calculation, which employs the formalism of Ref. 9 but which is independent of the above assumption, are presented.

The firm predictions of this theory are *relations*

among the transport coefficients. To extract the individual transport coefficients from these relations, assumptions must be made about the way in which the thermal conduction mode enters. Thus, the only information that this theory gives are these relations, unless we know from experiment the behavior of one or more of the transport coefficients.

A. Firm Relations Among Transport Coefficients

The firm prediction of the detailed analysis relating the anomalous part of the diffusion coefficient and η^* is

$$\eta^*[D(\vec{q}, s)] \Big|_{\text{singular}} \sim (\xi\beta)^{-1} \quad (3)$$

for $q \lesssim \xi^{-1}$ and $s \lesssim s\eta^*$. This relation corresponds to Eq. (3.27) of Ref. 9 which gives $\lambda/\rho C_P$ in terms of η^* for the liquid-gas transition.

According to the detailed theory, there is also an equation connecting D^* and the dominant singular contribution to η in the frequency range $s \lesssim s_D^*$; namely,

$$D^*[\eta(\vec{q}, s)] \Big|_{\text{singular}} \sim (\xi\beta)^{-1} \quad (4)$$

for $q \lesssim \xi^{-1}$. The derivation of (4) follows that which led to Eq. (3.19) of Ref. 9 for the connection between η and $\lambda^*/\rho C_P$ in the liquid-gas case. Equation (4) describes a result which is essentially similar to that obtained by earlier authors,^{1,2,5,8} save that we have not assumed the Ornstein-Zernike form for the static correlation functions, nor that $D \sim (\partial\mu_{12}/\partial x)_{P,T}$ in deriving it.

Finally our analysis predicts that the singular part of the bulk viscosity and D^* are related by

$$D^*[(\xi + \frac{4}{3}\eta)(\vec{q}, s)] \Big|_{\text{singular}} \sim \xi^{-1} k_B c^2 \left(\frac{1}{C_V} - \frac{1}{C_P} \right) \times \left\{ T \left(\frac{\partial\mu_{12}}{\partial x} \right)_{PT} \frac{\partial}{\partial T} \left[\left(\frac{\partial x}{\partial\mu_{12}} \right)_{P,T} \right]_{x,S/M} \right\}^2 \quad (5)$$

for $s \lesssim s_D^*$ and $q \lesssim \xi^{-1}$. In Eq. (5), c is the sound velocity, k_B is Boltzmann's constant, and C_V and C_P are the constant-volume and -pressure heat capacities, respectively. The contribution to the bulk viscosity described by (5) is essentially that calculated by Kawasaki and Tanaka⁷ save that again we have used the scaling laws to estimate correlation functions and have not assumed a specific form for D^* . Equation (5) also corresponds to the singular sound-wave damping constant in the liquid-gas case given by Kadanoff and Swift⁹ in their Eq. (3.24).

We emphasize again that equations of the type (3), (4), and (5) are the only ones, without any information from experiment, that our theory gives.

B. The Thermal Mode

If (3) and (4) described the only singular con-

tributions to D and η , we could employ the analysis of Ref. 9 to derive (1) and (2). However, there is a possible pitfall in the derivation of (1) and (2) from (3) and (4): the heat-conduction mode. To see this we have to consider the operators which enter the analysis in some detail. In a mixture there are two variables, the entropy and the concentration, which obey diffusion equations. To use the scheme of Ref. 9 we must take proper linear combinations of the operators representing these quantities so as to obtain an orthogonal set of local equilibrium states.

One of these operators, $x_{\text{op}} = (n_{1\text{op}}/\langle n_1 \rangle) - (n_{2\text{op}}/\langle n_2 \rangle)$, represents the concentration as its autocorrelations are related to $(\partial x/\partial\mu_{12})_{P,T}$ while the autocorrelations of its current yield the diffusion coefficient. The other operator whose average obeys a diffusion equation is then

$$s_{\text{op}}(\vec{q}) = \frac{\langle |s_{\text{op}}(-\vec{q})x_{\text{op}}(\vec{q})| \rangle}{\langle |x_{\text{op}}(-\vec{q})x_{\text{op}}(\vec{q})| \rangle} x_{\text{op}}(\vec{q})$$

in the notation of Ref. 9. Here s_{op} is the usual entropy operator; i. e., $Ts_{\text{op}} = (\text{energy density operator}) - (\text{average enthalpy per unit mass}) \times (\text{density operator})$. The above operator has autocorrelations which are related to C_p while its current-current correlation function gives $\lambda/\rho C_p + Dk_T^2(\partial\mu_{12}/\partial x)_{P,T}/TC_p$ where k_T is the thermal diffusion ratio.¹⁴

If the ratio $\langle |s_{\text{op}}(-\vec{q})x_{\text{op}}(\vec{q})| \rangle / \langle |x_{\text{op}}(-\vec{q})x_{\text{op}}(\vec{q})| \rangle$ remains substantially independent²⁵ of q for $q \lesssim \xi^{-1}$, the "thermal" operator given above never mixes with $x_{\text{op}}(\vec{q})$ at any point in the calculation so that (1) and (2) can be derived. With this assumption the thermal conductivity is found to have no divergent part, in apparent agreement with experiment. The thermal diffusion coefficient is found to have the singular part

$$(Dk_T)(\vec{q}, s) \sim |T - T_c|^{(2\nu - \alpha - \gamma)/2} \quad (6)$$

for $s \lesssim s\eta^*$ and $q \lesssim \xi^{-1}$ and the concentration having its critical value. Since the exponent²⁵ in (6) is probably within one or two tenths of zero, this describes at most a weak divergence Dk_T .

However, if

$$\frac{\partial \langle |s_{\text{op}}(-\vec{q})x_{\text{op}}(\vec{q})| \rangle}{\partial q} \frac{\langle |s_{\text{op}}(\vec{q})x_{\text{op}}(\vec{q})| \rangle}{\langle |x_{\text{op}}(-\vec{q})x_{\text{op}}(\vec{q})| \rangle} \sim \xi \frac{\langle |s_{\text{op}}(\vec{q})x_{\text{op}}(\vec{q})| \rangle}{\langle |x_{\text{op}}(\vec{q})x_{\text{op}}(\vec{q})| \rangle}$$

for $q \lesssim \xi^{-1}$ then the "thermal" operator will mix with $x_{\text{op}}(\vec{q})$ in the calculation. We note that Kawasaki⁵ has discussed a similar point. If also the entropy operator contains the large fluctuations in x_{op} , as is indicated by a mean field theory calculation, the analysis which led to (1) and (2) breaks down since the thermal conduction mode enters in an essential way. In this case we find that both $\lambda/\rho C_P$ and η exhibit strong divergences of the form $|T - T_c|^{(\nu - \gamma + \alpha)/2} \approx |T - T_c|^{-1/3}$ when the concentration has its critical value. Since this result for λ is in apparent disagreement with experiment,¹⁰ we consider it unlikely that the thermal conduction mode enters the problem.

C. Conclusions

With the above piece of information from experiment, the more detailed theory yields the results (1) and (2) so that our analysis predicts that η has at most a very weak divergence while D goes to zero only as fast as ξ^{-1} and not as $(\partial\mu/\partial x)_{P,T}$. The detailed analysis gives the result that λ should have no divergent part while Dk_T should have a singular part described by (6).

Finally, Eq. (5), where Eq. (2) is to be used for D^* , gives the singular part of the bulk viscosity which enters into the sound-wave damping constant.

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Critical-Point Behavior of a Model Describing a System of Interacting Fermions

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An analysis is given of the critical-point behavior of the two-parameter model which was previously shown to yield results which agree with He^3 data for the second virial coefficient and for the coexistence curve. The critical-point exponents of the model are calculated and found to be the same as those for a classical van der Waals gas. With the exception of the exponent characterizing the specific-heat singularity, the results agree reasonably well with published data on He^3 .

I. INTRODUCTION

In a previous paper¹ a study was made of a model which describes a system of interacting

fermions at densities and temperatures for which condensation of the gas could take place. The key point of this model involves the usage of a certain soluble model Hamiltonian,² which as shown by