

Statics and Dynamics in Binary Mixtures near the Liquid–Vapor Critical Line

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Static and dynamic properties are investigated near the liquid–vapor critical line in fluid binary mixtures. Simple expressions are given for thermodynamic derivatives and transport coefficients in terms of parameters characterizing the coexistence surface in the p - T - Δ space, where Δ is the chemical potential difference. It becomes possible to understand special crossover phenomena occurring when fluids are nearly azeotropic or when the concentration dependence of the critical temperature $T_c(X)$ [or the critical pressure $p_c(X)$] is weak. The results are used to explain recent data on ^3He - ^4He mixtures that apparently contradict previous theories. As a by-product, general relations are found for correlation functions of dynamic variables and thermodynamic derivatives in fluid mixtures.

1. INTRODUCTION

Static and dynamic critical phenomena have been studied extensively in pure fluids near the liquid–vapor critical point^{1–3} and in binary mixtures near the consolute (liquid–liquid) critical point.⁴ In two-component fluids there are also gas–liquid and gas–gas equilibria. There are no absolute differences among these three types of phase transitions. The geometry of the coexistence surfaces and the critical lines is in general very complicated in two-component fluids.^{3,5,6} As visualized in the three-dimensional space of three independent field variables, the coexistence surfaces terminate at the critical lines, and in the neighborhood of each critical point thermodynamic derivatives exhibit critical singularities and their asymptotic critical behavior can be predicted by phenomenological theories.^{7–9}

This paper studies static and dynamic properties near liquid–vapor critical points, which are called plait points, in fluid binary mixtures. In particular, I hope to explain data on ^3He - ^4He mixtures obtained by the Duke group,^{10–17} which apparently contradict Griffiths and Wheeler's

theory^{8,9} and general predictions of dynamic properties by Mistura.¹⁸ For other fluid mixtures near plait points data are not sufficient.^{3,19} In particular, those of transport properties are lacking. The experimental results on ³He-⁴He are summarized as follows.

1. The specific heat C_{pX} and the compressibility K_{TX} grow strongly like C_p and K_T in pure fluids on approaching the plait point.¹⁰ They saturate to constants typically at $T/T_c - 1 \approx 10^{-2}$ on the critical isochore. Here X denotes the ³He molar concentration. These thermodynamic derivatives have a weak singularity with the critical exponent α in usual binary mixtures near consolute critical points.⁴

2. The specific heat C_{vX} grows weakly like C_v in pure fluids in the whole measured temperature region.¹¹ It is expected to be virtually a constant near the usual consolute critical points.

3. With regard to the transport coefficients,^{14,15} the thermal conductivity κ and the thermodiffusion ratio k_T grow strongly as ξ and ξ^2 , respectively, where ξ is the correlation length and is given by $\xi_0(T/T_c - 1)^{-\nu}$ on the critical isochore, with $\xi_0 \approx 2 \text{ \AA}$ and $\nu \approx 0.63$. According to mode-coupling theory¹⁸ and renormalization-group theory,²⁰ κ should be finite and k_T should be of the order of ξ . This prediction is in accord with measurements in binary mixtures near consolute critical points, such as nitrobenzene-hexane²¹ or aniline-cyclohexane.²² The measured temperature region was $T/T_c - 1 \geq 7 \times 10^{-4}$ in the ³He-⁴He case and no crossover was observed. Furthermore, the thermal relaxation time in ³He-⁴He is nearly the same as that of pure ³He.²³

In this paper it is stressed that ³He-⁴He mixtures are nearly azeotropic^{5,7,8} along the liquid-vapor critical line at any concentration. This fact has not been emphasized explicitly, but it can be a guiding principle in analyzing data. Let us choose the pressure p , the temperature T , and the chemical potential difference $\Delta = \mu_3 - \mu_4$ as independent field variables. At a critical azeotropic point the normal to the coexistence surface (CXS) is orthogonal to the Δ axis. Near this point the concentration susceptibility $(\partial X/\partial \Delta)_{pT}$ does not grow strongly.^{7,8} In ³He-⁴He mixtures critical azeotropy does not occur, but the normal to CXS is nearly orthogonal to the Δ axis at any X .

The degree of azeotropy can be represented by a dimensionless parameter α_2 defined by

$$\alpha_2 = -n^{-1}(\partial p/\partial \Delta)_{T,CXS} \quad (1)$$

where n is the number density* and the derivative is taken on CXS with T

*Near the critical line one can set n equal to the critical density n_c . On CXS it can be defined as the average of the densities in the two phases.

fixed. Note that the normal to CXS is parallel to the vector

$$(1, -(\partial p/\partial T)_{\Delta, \text{CXS}}, -(\partial p/\partial \Delta)_{T, \text{CXS}})$$

in the p - T - Δ space. The azeotropic line is the locus of points on CXS along which $\alpha_2 = 0$. From the Gibbs-Duhem relation the differences of X and $V = n^{-1}$ in the two-phase state are related by $\Delta X = -\alpha_2 \Delta V / V \approx \alpha_2 \Delta n / n$ [see Eq. (56)]. Near plait points one expects $|\alpha_2| \leq 1$. The reverse case $|\alpha_2| \geq 1$ will be realized near consolute critical points. In ${}^3\text{He}$ - ${}^4\text{He}$ it will be found that

$$\alpha_2 \approx -\frac{1}{3}X(1-X) \quad (2)$$

I also show that the background part of $k_B T(\partial X/\partial \Delta)_{pT}$ is of order $X(1-X)$ in ${}^3\text{He}$ - ${}^4\text{He}$ and the growing part is of order $\alpha_2^2(T/T_c - 1)^{-\gamma}$ on the critical isochore. Thus one obtains a crossover reduced temperature t_{s1} defined by

$$t_{s1}^\gamma \approx \alpha_2^2 / X(1-X) \approx 10^{-1}X(1-X) \quad (3)$$

K_{TX} and C_{pX} cross over at $T/T_c - 1 \approx t_{s1}$. On the other hand, $t_{s1} \approx 1$ near the usual consolute critical points.

The isothermal diffusion constant D is equal to $(k_B T)^{-1} K_{22}(\partial \Delta/\partial X)_{pT}$, where K_{22} is an Onsager kinetic coefficient. K_{22} will be shown to be composed of a background part K_{22}^0 and a singular part,

$$K_{22} = K_{22}^0 + \alpha_2^2(k_B T/6\pi\eta\xi)R \quad (4)$$

Here η is the shear viscosity, $R \approx (T/T_c - 1)^{-\gamma}$ on the critical isochore, and $K_{22}^0 \approx D_0 X(1-X)$, with D_0 the background value of D . Equating the two terms in (4) yields a dynamic crossover reduced temperature t_D as

$$t_D^{-\nu} \approx \alpha_2^2(k_B T/6\pi\eta\xi_0 K_{22}^0) \approx (k_B T/6\pi\eta\xi_0 D_0)t_{s1}^\gamma \quad (5)$$

Roughly, $t_D \approx t_{s1}^2$ and t_D is typically of order 10^{-4} . The thermal conductivity κ and the thermodiffusion ratio k_T should cross over at $T/T_c - 1 \approx t_D$. Again, $t_D \approx 1$ near usual consolute critical points.

To explain the behavior of C_{vX} , another crossover reduced temperature t_{s2} must be introduced. Note that, if $dT_c/dX = 0$ (or $dT_c/d\Delta = 0$),⁸ C_{vX} diverges at $(T - T_c)^{-\alpha}$. Therefore, if $|dT_c/dX|$ is small, C_{vX} crosses over into a constant only close to the critical point. Define a dimensionless parameter β_2 by

$$\beta_2 = -k_B \left(\frac{dT}{d\Delta} \right)_c \left[1 - \frac{\Delta_c}{T_c} \left(\frac{dT}{d\Delta} \right)_c \right]^{-1} = \zeta(1-\zeta) \frac{1}{T_c} \left(\frac{dT}{d\zeta} \right)_c \quad (6)$$

where the derivative is along the critical line and $\zeta \equiv [1 + \text{const} \cdot \exp(\Delta/k_B T)]^{-1}$.⁹ In ${}^3\text{He}$ - ${}^4\text{He}$

$$\beta_2 \approx \frac{1}{2}X(1-X) \quad (7)$$

On the critical isochore, C_{VX} behaves as

$$C_{VX} \approx \text{const} \cdot (T/T_c - 1)^{-\alpha} / [\beta_2^2 (T/T_c - 1)^{-\alpha} + C_B] \quad (8)$$

where C_B is of the order of the background part of $k_B T (\partial X / \partial \Delta)_{pT}$ and is of order $X(1-X)$ in ${}^3\text{He}$ - ${}^4\text{He}$. Thus one finds

$$t_{s2}^\alpha \approx \beta_2^2 / X(1-X) \approx 0.2X(1-X) \quad (9)$$

Thus t_{s2} is strongly dependent on β_2 and is extremely small in ${}^3\text{He}$ - ${}^4\text{He}$ mixtures. On the other hand, if $|\beta_2| \geq 1$ at intermediate concentrations, t_{s2} is of order one and the corresponding crossover occurs quickly. This should be the case near usual consolute critical points.

In the dilute case $X \ll 1$ Anisimov *et al.*²⁴ found that the thermodynamic derivatives cross over at two reduced temperatures determined by $(T/T_c - 1)^\alpha \approx X$ and $(T/T_c - 1)^\gamma \approx X$. This is equivalent to the present result, because $t_{s1} \propto X^{1/\gamma}$ and $t_{s2} \propto X^{1/\alpha}$ as $X \rightarrow 0$.

In ${}^3\text{He}$ - ${}^4\text{He}$ the absolute values of α_2 and β_2 are both considerably smaller than one. As a consequence, $t_{s2} \ll t_D \ll t_{s1} \ll 1$. In CO_2 - C_2H_4 there is a critical azeotropic point and $\beta_2 \approx 0.1X(1-X)$.²⁵ Namely, $0 < \beta_2 \ll 1$ for any X . In CO_2 - C_2H_6 ,^{3,19,26} there is a critical azeotropic point and also a minimum point of T_c (at which $\beta_2 = 0$). In this fluid $|\beta_2| \ll 1$ for any X . Theoretically, however, there can be a fluid mixture with $|\alpha_2| \ll 1$ and $|\beta_2| \geq 1$, in which case T_c must be strongly dependent on X . In such a case $t_{s1} \ll t_{s2}$.

Griffiths and Wheeler's theory also means that the adiabatic compressibility $n^{-1}(\partial n / \partial p)_{sX}$ (or the sound velocity c_1) behaves as in pure fluids if $(dp/dX)_c = 0$. Denoting the crossover reduced temperature of this quantity by t_{s3} , it will be shown that

$$t_{s3}^\alpha = \left[\left(\frac{dp}{dT} \right)_c / \left(\frac{\partial p}{\partial T} \right)_{\Delta, \text{CXS}} \right]^2 t_{s2}^\alpha \quad (10)$$

In ${}^3\text{He}$ - ${}^4\text{He}$, $t_{s3} \approx t_{s2}$ and it is not necessary to introduce t_{s3} .

Leung and Griffiths (LG) presented an elegant thermodynamic model for ${}^3\text{He}$ - ${}^4\text{He}$ mixtures along the liquid-vapor critical line.⁹ Any thermodynamic derivatives can be calculated from this model. However, in most cases their expressions are complicated and numerical calculations are required. They showed numerically that K_{TX} and C_{VX} cross over very close to the critical line. The aim of this paper is to show more explicitly and quantitatively the origin of the crossover phenomena in statics and dynamics.

This paper is organized as follows. In Section 2 I first derive some general relations among thermodynamic derivatives and correlation functions of density variables.^{7,27} They indicate the magnitude of thermal fluctuations of the dynamic variables. Second I give approximations for thermo-

dynamic derivatives in terms of parameters such as α_2 and β_2 . They become very simple for ${}^3\text{He}$ - ${}^4\text{He}$ mixtures because $|\alpha_2| \ll 1$ and $|\beta_2| \ll 1$. In Section 3 dynamic properties are examined on the basis of mode-coupling theory.^{18,28}

2. STATICS

2.1. Fluctuations and Thermodynamic Derivatives

As fundamental dynamic variables in ${}^3\text{He}$ - ${}^4\text{He}$ mixtures I introduce the energy density $\hat{\varepsilon}(\mathbf{r})$, the ${}^3\text{He}$ number density $\hat{n}_3(\mathbf{r})$, and the ${}^4\text{He}$ number density $\hat{n}_4(\mathbf{r})$.* These variables have well-defined microscopic expressions. Hereafter quantities with a caret are dynamic variables (or operators in the quantal case) and those without a caret are thermodynamic quantities or simply constants. For example, the averages of the above variables over the canonical distribution are the usual thermodynamic density variables denoted by

$$u = \langle \hat{\varepsilon}(\mathbf{r}) \rangle, \quad n_3 = \langle \hat{n}_3(\mathbf{r}) \rangle, \quad n_4 = \langle \hat{n}_4(\mathbf{r}) \rangle \quad (11)$$

I will show that $\hat{\varepsilon}$, \hat{n}_3 , and \hat{n}_4 all exhibit strong critical fluctuations near the liquid-vapor critical line. To see this it is convenient to introduce the following notation:

$$\langle \hat{A} : \hat{B} \rangle = \int d\mathbf{r} \langle \delta \hat{A}(\mathbf{r}) \delta \hat{B}(\mathbf{0}) \rangle \quad (12)$$

where $\hat{A}(\mathbf{r})$ and $\hat{B}(\mathbf{r})$ represent some local variables (or some density variables), $\delta \hat{A} \equiv \hat{A} - \langle \hat{A} \rangle$, and $\delta \hat{B} \equiv \hat{B} - \langle \hat{B} \rangle$, and the average is over the equilibrium canonical distribution. The quantity $\langle \hat{A} : \hat{B} \rangle$ will be called the variance of \hat{A} and \hat{B} .† I also define the following field variables

$$\omega = p/k_B T, \quad B = 1/k_B T, \quad \nu_3 = \mu_3/k_B T, \quad \nu_4 = \mu_4/k_B T \quad (13)$$

where p is the pressure, μ_3 and μ_4 are the chemical potentials of ${}^3\text{He}$ and ${}^4\text{He}$ molecules, and k_B is the Boltzmann constant. Leung and Griffiths chose ω as a potential and B , ν_3 , and ν_4 as independent field variables. For this choice the second derivatives of ω are just equal to the variances of $\hat{\varepsilon}$, \hat{n}_3 , and \hat{n}_4 (see Appendix A). Namely,

$$\langle \hat{\varepsilon} : \hat{\varepsilon} \rangle = \frac{\partial^2 \omega}{\partial B^2} = -\frac{\partial u}{\partial B} \quad (14)$$

$$\langle \hat{\varepsilon} : \hat{n}_j \rangle = -\frac{\partial^2 \omega}{\partial B \partial \nu_j} = \frac{\partial u}{\partial \nu_j} = -\frac{\partial n_j}{\partial B} \quad (15)$$

*The following result can be used for any fluid binary mixtures.

†In the following I treat dynamic variables as scalar quantities in the framework of classical mechanics. In the quantal case the variance in (12) should be redefined as the space integral of the so-called canonical correlation in Kubo's sense.³¹

$$\langle \hat{n}_i : \hat{n}_j \rangle = \frac{\partial^2 \omega}{\partial v_i \partial v_j} = \frac{\partial n_i}{\partial v_j} = \frac{\partial n_j}{\partial v_i} \quad (16)$$

where $i, j = 3, 4$ and use has been made of the relation

$$d\omega = -u dB + n_3 dv_3 + n_4 dv_4 \quad (17)$$

Since $\langle A : A \rangle > 0$ unless $\hat{A} = 0$, (14)-(16) ensure that the potential ω is a concave function of the fields $-B$, v_3 , and v_4 , which is consistent with the requirements of thermodynamic stability.

The choice of B , v_3 , and v_4 as independent field variables appears to be most natural theoretically,^{1-3,8,32} but is rather unusual because v_3 and v_4 usually are not observable. The usual field variables are the pressure p , the temperature T , and the chemical potential difference $\Delta = \mu_3 - \mu_4$. The corresponding potential is μ_4 and the Gibbs-Duhem equation is

$$d\mu_4 = -s dT - X d\Delta + (1/n) dp \quad (18)$$

where s is the entropy per particle, X is the ^3He molar concentration, and n is the number density. Since $u + p - Tns$ is equal to the Gibbs free energy per unit volume, one obtains

$$u = n_3\mu_3 + n_4\mu_4 - p + Tns \quad (19)$$

From the definition of X one also has

$$n_3 = Xn, \quad n_4 = (1 - X)n \quad (20)$$

Not enough attention has been paid to the fact that one can introduce naturally the entropy variable \hat{s} (per particle) and the concentration variable \hat{X} as "linear combinations of $\hat{\epsilon}$, \hat{n}_3 , and \hat{n}_4 ," by²⁹

$$\hat{s} = \frac{1}{nT} (\hat{\epsilon} - T\hat{n} - \mu_3\hat{n}_3 - \mu_4\hat{n}_4) + \frac{p}{nT} + s \quad (21)$$

$$\hat{X} = X + \frac{1}{n} [(1 - X)\hat{n}_3 - X\hat{n}_4] \quad (22)$$

The coefficients and the constant terms in (21) and (22) are dependent on T , Δ , and p , but they smoothly tend to well-defined limits on approaching the critical line. From (19) and (20) one readily finds $\langle \hat{s} \rangle = s$ and $\langle \hat{X} \rangle = X$. Here I define the (total) number density variables \hat{n} by

$$\hat{n} = \hat{n}_3 + \hat{n}_4 \quad (23)$$

Then \hat{n}_3 and \hat{n}_4 can be expressed in terms of $\delta\hat{X} = \hat{X} - X$ and \hat{n} as

$$\hat{n}_3 = X\hat{n} + n\delta\hat{X}, \quad \hat{n}_4 = (1 - X)\hat{n} - n\delta\hat{X} \quad (24)$$

In Appendix A I prove the following relations²⁹:

$$\begin{aligned}
 n\langle\hat{s}:\hat{s}\rangle &= k_B C_{p\Delta}, & n\langle\hat{s}:\hat{X}\rangle &= k_B T \left(\frac{\partial X}{\partial T}\right)_{p\Delta} \\
 n\langle\hat{X}:\hat{X}\rangle &= k_B T \left(\frac{\partial X}{\partial \Delta}\right)_{pT}, & n\langle\hat{s}:\hat{n}\rangle &= k_B T \left(\frac{\partial n}{\partial T}\right)_{p\Delta} \\
 n\langle\hat{X}:\hat{n}\rangle &= k_B T \left(\frac{\partial n}{\partial \Delta}\right)_{pT}, & \langle\hat{n}:\hat{n}\rangle &= nk_B T \left(\frac{\partial n}{\partial p}\right)_{T\Delta}
 \end{aligned} \tag{25}$$

The relation (18) means that the variances among \hat{s} , \hat{X} , and \hat{n} are proportional to the second derivatives of $\mu_4(T, \Delta, p)$, which ensures the concaveness of μ_4 .

I stress the following two points. (1) The coefficients in the definitions of \hat{s} and \hat{X} are nearly nonsingular. If density variables were introduced as linear combinations of $\hat{\epsilon}$, \hat{n}_3 , and \hat{n}_4 with coefficients diverging or going to zero as $T \rightarrow T_c$, they could be useful in the hydrodynamic region $k\xi \ll 1$, but would give rise to confusion in the kinetic region $k\xi \geq 1$, where k is a typical wave number in the process under consideration. In this sense \hat{s} and \hat{X} are appropriate dynamic variables in the whole wave number region. (2) Because of (25), \hat{s} and \hat{X} are very natural and convenient for the study of both statics and dynamics. Moreover, nonequilibrium averages of \hat{s} and \hat{X} relax diffusively and their time scales are much shorter than that of the sound mode at long wavelengths. This also greatly simplifies the dynamic equations in terms of \hat{s} and \hat{X} .

Note that the derivatives in (14)–(16) and (25) are those of a density with respect to a field with the other two fields held fixed. In general they diverge strongly as $T \rightarrow T_c$ with the critical exponent γ if the normal to the coexistence surface (CXS) at the critical point under consideration is not orthogonal to any coordinate axis (or if no axis is parallel to CXS). Other types of derivatives can be expressed in terms of the variances as follows. As a first example consider the isothermal compressibility $K_{TX} = (1/n)(\partial n/\partial p)_{TX}$ at constant X . Use of the relations

$$\left(\frac{\partial n}{\partial p}\right)_{TX} = \left(\frac{\partial n}{\partial p}\right)_{T\Delta} + \left(\frac{\partial n}{\partial \Delta}\right)_{Tp} \left(\frac{\partial \Delta}{\partial p}\right)_{TX} \tag{26}$$

$$\left(\frac{\partial \Delta}{\partial p}\right)_{TX} = -\left(\frac{\partial X}{\partial p}\right)_{T\Delta} / \left(\frac{\partial X}{\partial \Delta}\right)_{Tp} \tag{27}$$

gives, from (25),

$$K_{TX} = (n^2 k_B T)^{-1} \left(\langle\hat{n}:\hat{n}\rangle - \frac{\langle\hat{n}:\hat{X}\rangle^2}{\langle\hat{X}:\hat{X}\rangle} \right) \tag{28}$$

Similarly, the specific heat $C_{pX} = T(\partial s/\partial T)_{pX}$ is written as

$$C_{pX} = (n/k_B)(\langle \hat{s} : \hat{s} \rangle - \langle \hat{s} : \hat{X} \rangle^2 / \langle \hat{X} : \hat{X} \rangle) \quad (29)$$

Griffiths and Wheeler's theory indicates that K_{TX} and C_{pX} in general diverge weakly asymptotically with the critical exponent α except for some accidental cases such as the azeotropic case (see below). This means that the strongly divergent parts of the variances on the right-hand sides of (28) and (29) cancel and vanish, but the weakly divergent parts remain.

Next I calculate derivatives with two densities held fixed, such as the specific heat $C_{nX} = T(\partial s/\partial T)_{nX}$. Define the following 3×3 symmetric matrix $\mathbf{\Omega} = \{\Omega_{ij}\}$ by

$$\Omega_{11} = \frac{\partial^2 \omega}{\partial B^2}, \quad \Omega_{1j} = -\frac{\partial^2 \omega}{\partial B \partial \nu_{j+1}}, \quad \Omega_{ij} = \frac{\partial^2 \omega}{\partial \nu_{i+1} \partial \nu_{j+1}} \quad (30)$$

where $i, j = 2, 3$. Then the inverse matrix $(\mathbf{\Omega})^{-1} = \{\Omega^{ij}\}$ can be expressed in terms of second derivatives of the entropy per unit volume $S = ns$ as

$$\begin{aligned} \Omega^{11} &= -k_B^{-1} \frac{\partial^2 S}{\partial u^2}, & \Omega^{1j} &= -k_B^{-1} \frac{\partial^2 S}{\partial u \partial n_{j+1}} \\ \Omega^{ij} &= -k_B^{-1} \frac{\partial^2 S}{\partial n_{i+1} \partial n_{j+1}} \end{aligned} \quad (31)$$

Here S is regarded as a function of the densities u , n_3 , and n_4 . This is obvious from the relation

$$k_B^{-1} dS = B du - \nu_3 dn_3 - \nu_4 dn_4 \quad (32)$$

In particular, from (32), the component Ω^{11} is related to the specific heat $C_{nX} = T(\partial s/\partial T)_{nX}$ by

$$\Omega^{11} = -(\partial B/\partial u)_{n_3, n_4} = (nk_B T^2 C_{nX})^{-1}. \quad (33)$$

On the other hand, Ω^{11} can be expressed in terms of Ω_{ij} as

$$\Omega^{11} = (\Omega_{22}\Omega_{33} - \Omega_{23}^2) / \text{Det } \mathbf{\Omega} \quad (34)$$

where $\text{Det } \mathbf{\Omega}$ is the determinant of $\mathbf{\Omega}$. Now consider the relation

$$\begin{aligned} \Omega_{22}\Omega_{33} - \Omega_{23}^2 &= \langle \hat{n}_3 : \hat{n}_3 \rangle \langle \hat{n}_4 : \hat{n}_4 \rangle - \langle \hat{n}_3 : \hat{n}_4 \rangle^2 \\ &= n^2 (\langle \hat{n} : \hat{n} \rangle \langle \hat{X} : \hat{X} \rangle - \langle \hat{n} : \hat{X} \rangle^2) \end{aligned} \quad (35)$$

The first line can be obtained from (16) and the second line from (24). Further, with the aid of (25) and (28), one can express $\text{Det } \mathbf{\Omega} =$

$(\Omega_{22}\Omega_{33} - \Omega_{23}^2)/\Omega^{11}$ in terms of the thermodynamic derivatives appearing so far:

$$\text{Det } \mathbf{\Omega} = n^3 k_B^3 T^5 \left(\frac{\partial X}{\partial \Delta} \right)_{pT} \left(\frac{\partial n}{\partial p} \right)_{TX} \left(\frac{\partial s}{\partial T} \right)_{nX} \quad (36)$$

This quantity diverges as $\propto (T - T_c)^{-\gamma-\alpha}$ on the critical isochore.

As noted by Griffiths and Wheeler, $\text{Det } \mathbf{\Omega}$ is the product of the three eigenvalues of $\mathbf{\Omega}$; one diverges strongly, another weakly, and the remaining one is finite. It is invariant with respect to the rotation of the coordinate axes in the field space, and hence its most singular part [which is proportional to $(T - T_c)^{-\gamma-\alpha}$ on the critical isochore] does not vanish in any case as long as $X \neq 0, 1$, for example, even if some axis is on CXS. In (102) $\text{Det } \mathbf{\Omega}$ will be calculated explicitly for $^3\text{He}-^4\text{He}$ mixtures on the basis of the LG model.

Using the Maxwell relations, one can rewrite the above product of the three thermodynamic derivatives into various different forms. For instance, use can be made of

$$(\partial n / \partial p)_{TX} (\partial s / \partial T)_{nX} = (\partial s / \partial T)_{pX} (\partial n / \partial p)_{sX}$$

Then the sound velocity c_1 can be expressed in a form exhibiting its critical behavior unambiguously. Because s and X relax diffusively (see Section 3), c_1^2 is given by the following derivative:

$$c_1^2 = \left(\frac{\partial p}{\partial \rho} \right)_{sX} = \frac{1}{\bar{M}} \left(\frac{\partial p}{\partial n} \right)_{sX} \quad (37)$$

where $\rho = \bar{M}n$ is the mass density and $\bar{M} = M_3X + M_4(1 - X)$ is the average mass, M_3 and M_4 being the ^3He and ^4He masses. Therefore,

$$c_1^2 = (n^3 k_B^3 T^4 / \bar{M}) (\partial X / \partial \Delta)_{pT} C_{pX} / (\text{Det } \mathbf{\Omega}) \quad (38)$$

In the same manner, the matrix $\mathbf{H} = \{H_{ij}\}$ is introduced by

$$H_{ij} = -\partial^2 \mu_4 / \partial a_i \partial a_j \quad (39)$$

where $a_1 \equiv T$, $a_2 \equiv \Delta$, and $a_3 \equiv p$. Then, from the relation $de = T ds + \Delta dX - p d(1/n)$, where e is the energy per particle, the inverse matrix $(\mathbf{H})^{-1} = \{H^{ij}\}$ is given by

$$H^{ij} = \partial^2 e / \partial b_i \partial b_j \quad (40)$$

where $b_1 \equiv s$, $b_2 \equiv X$, and $b_3 \equiv -1/n$. It is easy to show that

$$H^{11} = (\partial T / \partial s)_{nX} = T / C_{nX}$$

$$H_{22}H_{33} - H_{23}^2 = (\partial X / \partial \Delta)_{pT} (\partial n / \partial p)_{TX} / n^2$$

and

$$\text{Det } \mathbf{H} = n^{-2} \left(\frac{\partial X}{\partial \Delta} \right)_{pT} \left(\frac{\partial n}{\partial p} \right)_{TX} \left(\frac{\partial s}{\partial T} \right)_{nX} = (n^5 k_B^3 T^5)^{-1} \text{Det } \mathbf{\Omega} \quad (41)$$

Any thermodynamic derivative can be expressed simply in terms of the elements of $\mathbf{\Omega}$ and $(\mathbf{\Omega})^{-1}$ [or those of \mathbf{H} and $(\mathbf{H})^{-1}$].^{8,29} For example, the Duke group measured $(\partial p / \partial T)_{nX}$ at $X = 0.805$.¹² This derivative can be expressed as

$$(\partial p / \partial T)_{nX} = H^{13} / H^{11} = (H_{12}H_{23} - H_{22}H_{31}) / (H_{22}H_{33} - H_{23}^2) \quad (42)$$

In terms of the variances one obtains

$$\begin{aligned} (\partial p / \partial T)_{nX} &= -n^2 (\langle \hat{s} : \hat{n} \rangle - \langle \hat{s} : \hat{X} \rangle \langle \hat{n} : \hat{X} \rangle / \langle \hat{X} : \hat{X} \rangle) \\ &\quad \times (\langle \hat{n} : \hat{n} \rangle - \langle \hat{n} : \hat{X} \rangle^2 / \langle \hat{X} : \hat{X} \rangle)^{-1} \end{aligned} \quad (43)$$

Note that any components of $(\mathbf{\Omega})^{-1}$ and $(\mathbf{H})^{-1}$ in general have a cusp and remain finite as $T \rightarrow T_c$.

2.2. Strongly Divergent Part of Variances

Let us first consider the most strongly divergent part of the variances. The coexistence surface (CXS) can be expressed in the space of the field variables in terms of a smooth function h as⁹

$$h(B, \nu_3, \nu_4) = 0 \quad (44)$$

The CXS terminates at the critical line, but here it is assumed that it may be extended smoothly into the region of the disordered phase. Griffiths and Wheeler's theory leads to

$$\frac{\partial^2 \omega}{\partial B^2} \sim \left(\frac{\partial h}{\partial B} \right)^2 R, \quad \frac{\partial^2 \omega}{\partial B \partial \nu_j} \sim \frac{\partial h}{\partial B} \frac{\partial h}{\partial \nu_j} R, \quad \frac{\partial^2 \omega}{\partial \nu_i \partial \nu_j} \sim \frac{\partial h}{\partial \nu_i} \frac{\partial h}{\partial \nu_j} R \quad (45)$$

The quantity R diverges strongly on approaching the critical line. The derivatives may be regarded to be those taken at the critical point under consideration.

Now from (14)–(16) one notices that, as long as the most singular parts of the variances are concerned, one can set

$$\hat{\varepsilon}(\mathbf{r}) \approx -\frac{\partial h}{\partial B} \hat{n}(\mathbf{r}), \quad \hat{n}_3(\mathbf{r}) \approx \frac{\partial h}{\partial \nu_3} \hat{n}(\mathbf{r}), \quad \hat{n}_4(\mathbf{r}) \approx \frac{\partial h}{\partial \nu_4} \hat{n}(\mathbf{r}) \quad (46)$$

Here, in other words, $\hat{\varepsilon}$, \hat{n}_3 , and \hat{n}_4 have been “projected” onto \hat{n} . One can

choose h without loss of generality such that

$$\frac{\partial h}{\partial \nu_3} + \frac{\partial h}{\partial \nu_4} = 1 \quad (47)$$

as in the case of LG. This relation holds if

$$h = \nu_3 - f(\nu_3 - \nu_4, B) \quad (48)$$

where f is the value of ν_3 on CXS as a function of $\nu_3 - \nu_4$ and B . The vector $(\partial h/\partial B, \partial h/\partial \nu_3, \partial h/\partial \nu_4)$ is the normal to CXS in the B, ν_3, ν_4 space and it will tend to a well-defined limit vector on approaching each critical point.

From (21) and (22) the most singular parts of \hat{s} and \hat{X} are expressed as

$$\hat{s} \approx k_B \alpha_1 n^{-1} \hat{n}, \quad \hat{X} \approx \alpha_2 n^{-1} \hat{n} \quad (49)$$

where

$$\alpha_1 = - \left(B \frac{\partial h}{\partial B} + \frac{s}{k_B} + \nu \frac{\partial h}{\partial \nu_3} + \nu_4 \frac{\partial h}{\partial \nu_4} \right) \quad (50)$$

$$\alpha_2 = (1 - X) \frac{\partial h}{\partial \nu_3} - X \frac{\partial h}{\partial \nu_4} \quad (51)$$

After some calculations, one also has

$$\alpha_1 = (nk_B)^{-1} \left(\frac{\partial h}{\partial T} \right)_{p\Delta} / \left(\frac{\partial h}{\partial p} \right)_{T\Delta} = - \frac{1}{nk_B} \left(\frac{\partial p}{\partial T} \right)_{\Delta, \text{CXS}} \quad (52)$$

$$\alpha_2 = n^{-1} \left(\frac{\partial h}{\partial \Delta} \right)_{pT} / \left(\frac{\partial h}{\partial p} \right)_{T\Delta} = - \frac{1}{n} \left(\frac{\partial p}{\partial \Delta} \right)_{T, \text{CXS}}$$

where h is regarded as a function of p, T , and Δ , and $(\partial/\partial T)_{\Delta, \text{CXS}}$ and $(\partial/\partial \Delta)_{T, \text{CXS}}$ are the derivatives on CXS. From (47)

$$\left(\frac{\partial h}{\partial p} \right)_{T\Delta} = \left(\frac{\partial \nu_3}{\partial p} \right)_{T\Delta} \frac{\partial h}{\partial \nu_3} + \left(\frac{\partial \nu_4}{\partial p} \right)_{T\Delta} \frac{\partial h}{\partial \nu_4} = \frac{1}{nk_B T} \quad (53)$$

This is because $dp/k_B T = n d\nu_3 = n d\nu_4$ if T and Δ are fixed. Therefore, the normal to CXS in the T, Δ, p space is proportional to the vector $(k_B n \alpha_1, n \alpha_2, 1)$.

In terms of α_1 and α_2 the asymptotic forms of the variances are expressed as

$$\begin{aligned} n\langle \hat{s} : \hat{s} \rangle &\approx k_B^2 \alpha_1^2 R, & n\langle \hat{s} : \hat{X} \rangle &\approx k_B \alpha_1 \alpha_2 R \\ n\langle \hat{X} : \hat{X} \rangle &\approx \alpha_2^2 R, & \langle \hat{s} : \hat{n} \rangle &\approx k_B \alpha_1 R, & \langle \hat{X} : \hat{n} \rangle &\approx \alpha_2 R \end{aligned} \quad (54)$$

where R is the dimensionless density variance defined by

$$R \equiv \langle \hat{n} : \hat{n} \rangle / n = k_B T (\partial n / \partial p)_{T\Delta} = n k_B T K_{T\Delta} \quad (55)$$

$K_{T\Delta}$ being the isothermal compressibility at constant Δ . Roughly speaking, the two constants α_1 and α_2 indicate how the fluctuations of \hat{s} and \hat{X} are parallel to that of \hat{n} .

Consider the averages s , X , and n in the two-phase state. Let Δs , ΔX , and Δn be the differences between the values of s , X , and n in the liquid phase and those in the gas phase. Then,

$$\Delta s = k_B \alpha_1 \Delta n / n_c \quad \Delta X = \alpha_2 \Delta n / n_c \quad (56)$$

where n_c is the critical density and $\Delta n \propto (T_c - T)^\beta$. The proof of (56) is as follows: In the two phases the field variables assume the same values. Hence, two closely separated points (T, Δ, p) and $(T + dT, \Delta + d\Delta, p + dp)$ on CXS are considered one finds from (18)

$$-(\Delta s) dT - (\Delta X) d\Delta + \Delta(1/n) dp = 0 \quad (57)$$

Therefore, the vector $(\Delta s, \Delta X, -\Delta(1/n))$ must be parallel to the normal to CXS. As will be shown below, $\alpha_1 \approx -1$ and $\alpha_2 \approx -\frac{1}{3}X(1-X)$ in ${}^3\text{He}$ - ${}^4\text{He}$ mixtures, so that the entropy (per particle or per mole) and the ${}^3\text{He}$ concentration are smaller in the liquid phase than in the gas phase. However, with regard to the entropy per unit volume $S = ns$, $\Delta S/S \approx (2/3)\Delta n/n$, since $s/k_B \approx 3$ for any X .⁹

Finally, consider the following intriguing exceptional case. A point on CXS is called an azeotropic point if the concentration is the same in the two phases.⁵ The locus of azeotropic points can reach the critical line, giving rise to a critical azeotropic point. This situation has been encountered in a number of fluid mixtures.^{3,25,26} Denote the angle between the Δ axis and the normal to CXS at each critical point by θ_Δ . Then,

$$\cos \theta_\Delta \propto \alpha_2 \quad (58)$$

The critical azeotropy occurs for $\alpha_2 = 0$ in the present notation. Here the Δ axis is on CXS and the concentration \hat{X} does not exhibit strong critical fluctuations. As a consequence, $(\partial X / \partial \Delta)_{pT}$ diverges at most weakly, while K_{TX} and C_{pX} diverge strongly as in pure fluids. It should also be noted that, if $|\alpha_2| \ll 1$ but $\alpha_2 \neq 0$, the fluid mixture is nearly azeotropic and the crossover from the pure fluid behavior to the mixture behavior should occur only very close to the critical point.

2.3. Weakly Divergent Part of Variances

To calculate explicitly derivatives such as K_{TX} , C_{pX} , or C_{nX} , the weakly divergent part of the variances must be further examined. To this end, the

following dimensionless variable is introduced:

$$\hat{M} = (nk_B T)^{-1} \left(\delta\hat{\varepsilon} - \frac{\langle \hat{\varepsilon} : \hat{n} \rangle}{\langle \hat{n} : \hat{n} \rangle} \delta\hat{n} \right) \quad (59)$$

where $\delta\hat{\varepsilon} = \hat{\varepsilon} - u$ and $\delta\hat{n} = \hat{n} - n$. This variable is orthogonal to \hat{n} (namely, $\langle \hat{M} : \hat{n} \rangle = 0$) and should have a weakly divergent variance. Define

$$U = n \langle \hat{M} : \hat{M} \rangle = n^{-1} (k_B T)^{-2} [\langle \hat{\varepsilon} : \hat{\varepsilon} \rangle - \langle \hat{\varepsilon} : \hat{n} \rangle^2 / \langle \hat{n} : \hat{n} \rangle] \quad (60)$$

This quantity has a particularly simple expression in the LG model (see Appendix B), and it behaves as $(T - T_c)^{-\alpha}$ on the critical isochore.

The density variables \hat{n}_3 and \hat{n}_4 can be expressed as

$$\hat{n}_3 = \alpha_3 \hat{n} + n\beta_3 \hat{M} + \dots, \quad \hat{n}_4 = \alpha_4 \hat{n} + n\beta_4 \hat{M} + \dots \quad (61)$$

where

$$\alpha_j = \langle \hat{n}_j : \hat{n} \rangle / \langle \hat{n} : \hat{n} \rangle \quad (62)$$

$$\beta_j = \langle (\hat{n}_j - \alpha_j \hat{n}) : \hat{M} \rangle / n \langle \hat{M} : \hat{M} \rangle \quad (63)$$

From the definition one finds

$$\alpha_3 + \alpha_4 = 1, \quad \beta_3 + \beta_4 = 0 \quad (64)$$

The terms not written explicitly in (61) are orthogonal to \hat{n} and \hat{M} and are assumed to have variances which remain finite as $T \rightarrow T_c$. This is surely the case within the LG approximation. Equation (45) requires

$$\alpha_3 \rightarrow \partial h / \partial v_3, \quad \alpha_4 \rightarrow \partial h / \partial v_4 \quad \text{as } T \rightarrow T_c \quad (65)$$

Then, from (21) and (22),

$$\delta\hat{s} / k_B = \alpha_1 \delta\hat{n} / n + \beta_1 \delta\hat{M} + \dots \quad (66)$$

$$\delta\hat{X} = \alpha_2 \delta\hat{n} / n + \beta_2 \delta\hat{M} + \dots \quad (67)$$

where

$$\alpha_1 = k_B n \langle \hat{s} : \hat{n} \rangle / \langle \hat{n} : \hat{n} \rangle$$

$$\alpha_2 = (1 - X)\alpha_3 - X\alpha_4 \quad (68)$$

$$\beta_1 = 1 - \nu_3 \beta_3 - \nu_4 \beta_4 = 1 - (\nu_3 - \nu_4) \beta_3$$

$$\beta_2 = (1 - X)\beta_3 - X\beta_4 = \beta_3 = -\beta_4 \quad (69)$$

The above definitions of α_1 and α_2 are not exactly the same as (50) and (51), but the difference vanishes as $T \rightarrow T_c$ due to (65). On the other

hand, β_1 and β_2 tend to the following limits as $T \rightarrow T_c$:

$$\beta_1 = \left[1 - \frac{\Delta_c}{T_c} \left(\frac{dT}{d\Delta} \right)_c \right]^{-1} + \dots \quad (70)$$

$$\beta_2 = -k_B \left(\frac{dT}{d\Delta} \right)_c \left[1 - \frac{\Delta_c}{T_c} \left(\frac{dT}{d\Delta} \right)_c \right]^{-1} + \dots$$

where the derivatives on the right-hand side are along the critical line and the terms not explicitly written go to zero as $T \rightarrow T_c$. These relations can be readily derived in the LG scheme, as shown in Appendix B. A general proof is given in Appendix C.

Now, up to the weakly divergent terms, the variances among $\delta\hat{s}$, $\delta\hat{X}$, and $\delta\hat{n}$ are written as

$$nk_B^{-2} \langle \hat{s} : \hat{s} \rangle = \alpha_1^2 R + \beta_1^2 U + \dots \quad (71)$$

$$nk_B^{-1} \langle \hat{s} : \hat{X} \rangle = \alpha_1 \alpha_2 R + \beta_1 \beta_2 U + \dots \quad (72)$$

$$n \langle \hat{X} : \hat{X} \rangle = \alpha_2^2 R + \beta_2^2 U + \dots \quad (73)$$

$$k_B^{-1} \langle \hat{s} : \hat{n} \rangle = \alpha_1 R + \dots \quad (74)$$

$$\langle \hat{X} : \hat{n} \rangle = \alpha_2 R + \dots \quad (75)$$

Note that α_1 and α_2 are nonanalytic functions of $T - T_c$. From (62) one expects the following form on the critical isochore:

$$\alpha_j = \lim_{T \rightarrow T_c} \alpha_j + \alpha_{j1} (T - T_c) + \alpha_{j2} (T - T_c)^{\gamma - \alpha} + \dots \quad (76)$$

Namely, there can be terms proportional to $(T - T_c)^{-\alpha}$ also on the right-hand sides of (74) and (75).

From (28) and (29) the derivatives K_{TX} and C_{pX} can be expressed as

$$K_{TX} = (nk_B T)^{-1} R (\beta_2^2 U + \dots) / (\alpha_2^2 R + \beta_2^2 U + \dots) \quad (77)$$

$$C_{pX} = k_B \alpha_1^2 R [(\beta_2 - \alpha_2 \beta_1 / \alpha_1)^2 U + \dots] / (\alpha_2^2 R + \beta_2^2 U + \dots) \quad (78)$$

In the same way the thermal expansion coefficient $(\partial n / \partial T)_{pX} / n$ is given by

$$\begin{aligned} & (\partial n / \partial T)_{pX} / n \\ & = T^{-1} \alpha_1 R [\beta_2 (\beta_2 - \alpha_2 \beta_1 / \alpha_1) U + \dots] / (\alpha_2^2 R + \beta_2^2 U + \dots) \end{aligned} \quad (79)$$

These three quantities are asymptotically proportional to U as $T \rightarrow T_c$. The background parts, which are not explicitly written in (77)–(79), are all nearly equal to the background part of $n \langle \hat{X} : \hat{X} \rangle$ in the nearly azeotropic case. Similarly, C_{nX} , (36), c_1^2 , (38), and $(\partial p / \partial T)_{nX}$, (43), are expressed as

$$C_{nX} = (\text{Det } \mathbf{\Omega} / n^3 k_B T^2 R) / (\beta_2^2 U + \dots) \quad (80)$$

$$c_1^2 = [(nk_B T)^3 \alpha_1^2 / \bar{M}] R[(\beta_2 - \alpha_2 \beta_1 / \alpha_1)^2 U + \dots] / \text{Det } \Omega \quad (81)$$

$$(\partial p / \partial T)_{nX} = -k_B n \alpha_1 [\beta_2 (\beta_2 - \alpha_2 \beta_1 / \alpha_1) U + \dots] / (\beta_2^2 U + \dots) \quad (82)$$

In C_{pX} , c_1^2 , $(\partial n / \partial T)_{pX}$, and $(\partial p / \partial T)_{nX}$ there appears the combination $\beta_2 - \alpha_2 \beta_1 / \alpha_1$, which can be related to $(dp/d\Delta)_c$ as follows. From (56) and (57), $k_B \alpha_1 dT + \alpha_2 d\Delta + n^{-1} dp = 0$ on CXS. In particular, along the critical line,

$$n^{-1} \left(\frac{dp}{d\Delta} \right)_c = -k_B \alpha_1 \left(\frac{dT}{d\Delta} \right)_c - \alpha_2 = \alpha_1 \beta_2 / \beta_1 - \alpha_2 \quad (83)$$

If $(dp/d\Delta)_c = 0$ [or $(dp/dX)_c = 0$], C_{pX} and c_1^2 do not saturate to constants in accord with the theoretical predictions.^{7,8} Thus the ratio of $\beta_2 - \alpha_2 \beta_1 / \alpha_1$ to β_2 can be written as

$$\frac{\beta_2 - \alpha_2 \beta_1 / \alpha_1}{\beta_2} = \left(\frac{dp}{d\Delta} \right)_c / \left(\frac{\partial p}{\partial T} \right)_{\Delta, \text{CXS}} \quad (84)$$

where use has been made of (52). In ^3He - ^4He the above ratio happens to be close to one [see (104)]. For other mixtures the absolute value of the above ratio can be much greater or much smaller than one. Then c_1 and C_{pX} cross over at another crossover reduced temperature t_{s3} defined by (10). The thermal expansion coefficient crosses over at $t_{s4} \equiv (t_{s2} t_{s3})^{1/2}$ from (79).

2.4. Approximations for ^3He - ^4He Mixtures

The chemical potential μ_3 (or μ_4) goes to $-\infty$ as $k_B T \ln X$ [or $k_B T \ln(1-X)$] as $X \rightarrow 0$ (or 1). Thus $\Delta \sim k_B T \ln[X(1-X)]$ in the dilute case. Therefore the overall structure of CXS can be visualized in the space of T , p , and⁹

$$\zeta \equiv 1/[1 + \text{const} \cdot \exp(\nu_3 - \nu_4)] \quad (85)$$

more easily than in the space of T , p , and Δ . Here $0 \leq \zeta \leq 1$; $\zeta = 1$ for pure ^3He and $\zeta = 0$ for pure ^4He . In ^3He - ^4He mixtures the CXS smoothly connects the coexistence lines of pure ^3He and ^4He in the T , p , ζ space. Note the relations

$$\left(\frac{\partial h}{\partial \Delta} \right)_{pT} = -(k_B T)^{-1} \zeta (1 - \zeta) \left(\frac{\partial h}{\partial \zeta} \right)_{pT} \quad (86)$$

$$\left(\frac{dT}{d\Delta} \right)_c = -(k_B T_c)^{-1} \zeta (1 - \zeta) \left[1 - \frac{\Delta_c}{T_c} \left(\frac{dT}{d\Delta} \right)_c \right] \left(\frac{dT}{d\zeta} \right)_c \quad (87)$$

where h is defined by (44) or (48) and the derivatives in the second relation

are taken along the critical line. We assume that $(\partial h/\partial \zeta)_{pT}$ and $(dT/d\zeta)_c$ have well-defined finite limits in the dilute case. In terms of these quantities α_2 , (52), and β_2 , (70), are written as

$$\alpha_2 = \zeta(1-\zeta)(nk_B T)^{-1} \left(\frac{\partial p}{\partial \zeta} \right)_{T, \text{CXS}} \quad (88)$$

$$\beta_2 \approx \zeta(1-\zeta) \frac{1}{T_c} \left(\frac{dT}{d\zeta} \right)_c \quad (89)$$

It is convenient to introduce α_c and β_c by

$$\alpha_2 = \alpha_c X(1-X) \quad (90)$$

$$\beta_2 = \beta_c X(1-X) \quad (91)$$

The main X dependence of α_2 and β_2 will be absorbed into the factor $X(1-X)$. Note that $\zeta \sim 1-X$ particularly in $^3\text{He}-^4\text{He}$.⁹

Figure 1 plots α_1 and α_c for $^3\text{He}-^4\text{He}$ mixtures along the critical line as functions of X . Use has been made of (50), (51), and the LG scheme.

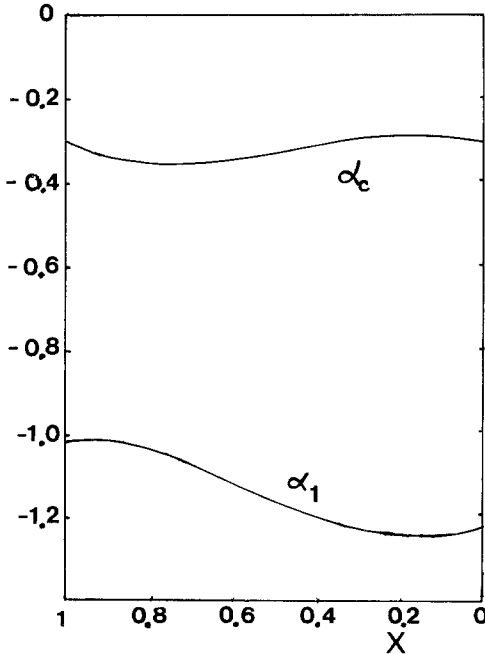


Fig. 1. The two parameters α_1 and α_c calculated from (50) and (51) using the Griffiths and Wheeler parametrization of CXS.

As a simple result, they are nearly constants at any X as

$$\alpha_1 \approx -1, \quad \alpha_c \approx -\frac{1}{3} \quad (92)$$

The fluctuation of \hat{s}/k_B is of the same order as that of \hat{n}/n , whereas the singular part of \hat{X} is very small. The concentration difference ΔX in the two-phase state is also very small, from (56). For example, $\alpha_2 = -0.083$ even at $X = \frac{1}{2}$. Now one can conclude that ${}^3\text{He}$ - ${}^4\text{He}$ mixture are nearly azeotropic at any X .

The following approximate expression is derived in Appendix B:

$$k_B T \left(\frac{\partial X}{\partial \Delta} \right)_{pT} = n(\hat{X} : \hat{X}) \approx C_0 X(1-X) + X^2(1-X)^2(\alpha_c^2 R + \beta_c^2 U) \quad (93)$$

where the first term is the background part with $C_0 \approx 1$ and R and U are defined by (55) and (60), respectively. On the critical isochore R and U are expressed as

$$R \approx R_0 t^{-\gamma}, \quad U \approx U_0 t^{-\alpha} \quad (94)$$

where R_0 and U_0 are constants and $t \equiv T/T_c - 1$ (not to be confused with the time variable). Figure 2 plots C_0 , R_0 , and A_0 along the critical line, where

$$A_0 \equiv \alpha_c^2 R_0 / C_0 \approx 0.06 \quad (95)$$

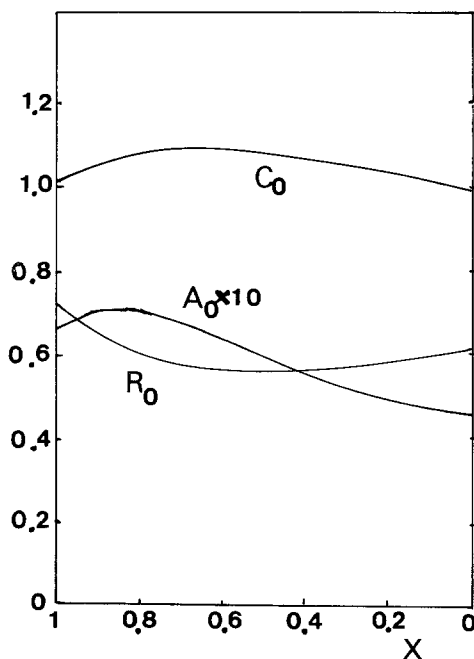


Fig. 2. The three constants C_0 in (93), R_0 in (94), and A_0 defined by (95). Note that A_0 is multiplied by ten.

In Figs. 3 and 4 the coefficients related to the weak singularity, β_1 , β_c , U_0 , and B_0 , are shown, where

$$B_0 \equiv \beta_c^2 U_0 / C_0 \quad (96)$$

Also in this case β_1 and β_c are weakly dependent on X as

$$\beta_1 \approx 1, \quad \beta_c \approx \frac{1}{2} \quad (97)$$

In (93) the weakly divergent term is negligible for $|t| \lesssim 1$ because of (97), and on the critical isochore

$$k_B T \left(\frac{\partial X}{\partial \Delta} \right)_{pT} \approx C_0 X(1-X) [1 + A_0 X(1-X)t^{-\gamma}] \quad (98)$$

Therefore one finds a small crossover reduced temperature t_{s1} defined by

$$t_{s1}^\gamma = A_0 X(1-X) \approx 0.06 X(1-X) \quad (99)$$

The susceptibility $(\partial X / \partial \Delta)_{pT}$ increases appreciably above the background value only for $|t| \ll t_{s1}$. Typically, $t_{s1} \approx 10^{-2}$ except for the dilute case, in accord with experiments.

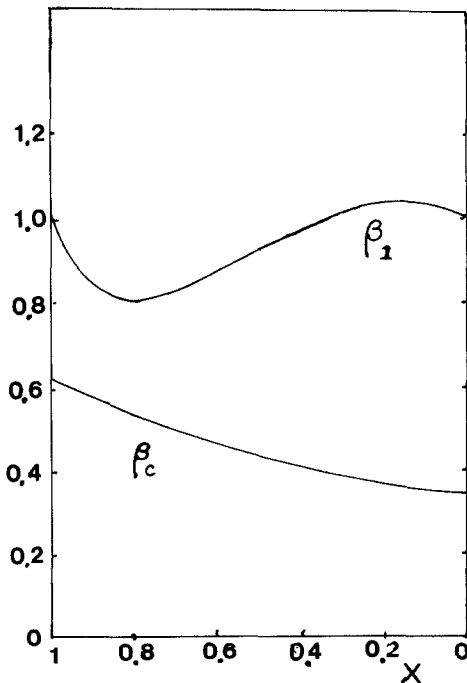


Fig. 3. The two parameters β_1 and β_c calculated from (70) and (89).

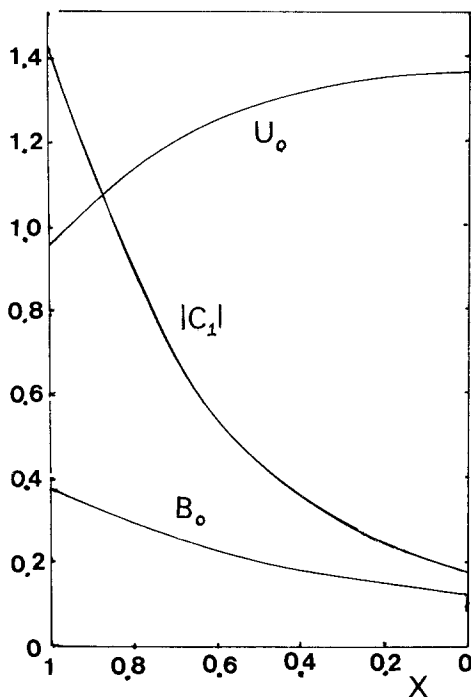


Fig. 4. The two parameters U_0 in (94) and B_0 defined by (96). In the GW scheme U is given by (B6).

Next from (77) the compressibility K_{TX} behaves as

$$K_{TX} \approx K_{T\Delta} [C_0 + \beta_c^2 X(1-X)U] / [C_0 + \alpha_c^2 X(1-X)R] \quad (100a)$$

$$\approx (R_0 / nk_B T) t^{-\gamma} [1 + B_0 X(1-X)t^{-\alpha}] / [1 + A_0 X(1-X)t^{-\gamma}] \quad (100b)$$

The second line is valid on the critical isochore. Thus there is another crossover reduced temperature t_{s2} defined by

$$t_{s2}^\alpha = B_0 X(1-X) \quad (101)$$

First K_{TX} grows as $K_{T\Delta}$ for $t \geq t_{s1}$. Then it saturates to the constant $C_0 / [\alpha_c^2 X(1-X)nk_B T]$ for $t_{s2} \leq t \leq t_{s1}$. Finally, it begins to increase slowly as $(\beta_c^2 / \alpha_c^2)U / nk_B T$ for $0 < t \leq t_{s2}$. The new crossover reduced temperature t_{s2} is extremely small. For example, $t_{s2} = 3 \times 10^{-13}$ even at $X = \frac{1}{2}$ if $\alpha = 0.1$. The second crossover is thus not observable in presently accessible experimental conditions. Figure 5 plots the product

$$F(t, X) \equiv n_c k_B T_c K_{TX} [1 + A_0 X(1-X)t^{-\gamma}]$$

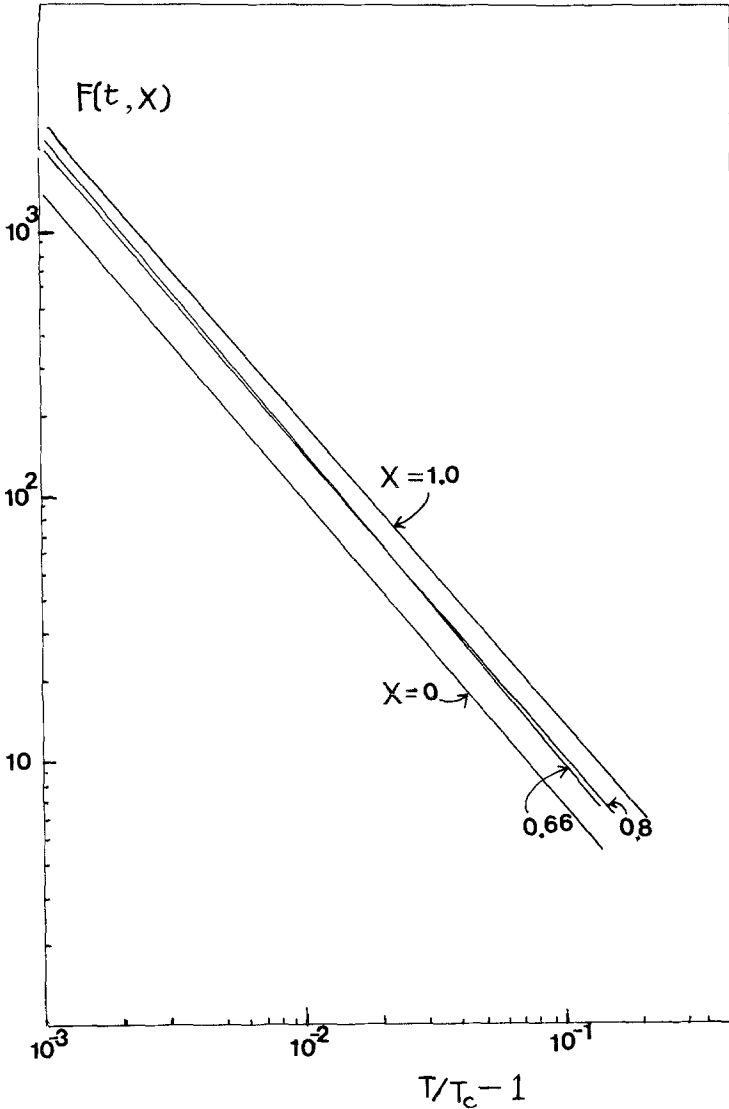


Fig. 5. Plot of $F(t, X) = n_c k_B T_c K_{TX} [1 + A_0 X(1-X)t^{-\gamma}]$ versus $t = T/T_c - 1$ on the critical isochore. Here use has been made of data of n_c , T_c , and K_{TX} in Ref. 15. This quantity should be nearly equal to $R_0 t^{-\gamma}$ for $t \gg t_{s2}$ from (100b).

with $\gamma = 1.16$, where the data of K_{TX} , n_c , and T_c are taken from Ref. 15 and A_0 is from Fig. 2. Evidently $F(t, X) \propto t^{-\gamma}$ at any X .

Leung and Griffiths also calculated the expression for Det Ω , (36). As will be shown in Appendix B, their result can be approximately rewritten as

$$\text{Det } \Omega \approx n^3(k_B T)^2 [C_0 X(1-X) + C_1 X^2(1-X)^2] R U \quad (102)$$

where C_1 is a negative number of order one and $|C_1|$ is plotted in Fig. 4. From (80) the specific heat C_{nX} behaves on the critical isochore as

$$C_{nX} \approx k_B U_0 t^{-\alpha} \left[1 + \frac{C_1}{C_0} X(1-X) \right] / [1 + B_0 X(1-X)t^{-\alpha}] \quad (103)$$

Thus C_{nX} crosses over only at $t \approx t_{s2}$; namely, $C_{nX} \propto U$ for $t_{s2} \leq t \ll 1$ and $C_{nX} \approx [k_B U_0 / B_0 X(1-X)]$ only for $t \leq t_{s2}$. This behavior is consistent with experiments. Using the data of Ref. 15, one finds $t^\alpha C_{nX} / k_B = 1.0-1.4$ at $t \approx 10^{-4}$ for any X , where $\alpha = 0.1$.

The second crossover of C_{pX} , (78), will also occur at $t \approx t_{s2}$. This is because, from Figs. 1 and 3,

$$\beta_2 - \alpha_2 \beta_1 / \alpha_1 = X(1-X)(\beta_c - \alpha_c \beta_1 / \alpha_1) \approx X(1-X)\beta_c = \beta_2 \quad (104)$$

Thus, if $t_{s2} \ll t \ll 1$, the ratio K_{TX} / C_{pX} is independent of t . With regard to c_1^2 and $(\partial p / \partial T)_{nX}$, (81) and (82), they cross over not at $t \approx t_{s1}$, but only at $t \approx t_{s2}$. Therefore, c_1^2 decreases as t^α and $(\partial p / \partial T)_{nX}$ appears to be regular in the present experimental conditions.

3. DYNAMICS

3.1. Hydrodynamic Equations

It is assumed that T and Δ deviate infinitesimally from their equilibrium values and change very slowly in space. The pressure is assumed to be constant in the fluid. Then their motion is described by the diffusion equations. For mathematical convenience, using the notation of Ref. 30, I define the following dimensionless variables:

$$m_1(\mathbf{r}, t) = \delta s(\mathbf{r}, t) / k_B, \quad m_2(\mathbf{r}, t) = \delta X(\mathbf{r}, t) \quad (105)$$

$$h_1(\mathbf{r}, t) = \frac{1}{T} \delta T(\mathbf{r}, t), \quad h_2(\mathbf{r}, t) = \frac{1}{k_B T} \delta \Delta(\mathbf{r}, t) \quad (106)$$

where δs , δX , δT , and $\delta \Delta$ are the deviations. The hydrodynamic equations are written as

$$\frac{\partial}{\partial t} m_i = \sum_{j=1}^2 K_{ij} \nabla^2 h_j \quad (107)$$

The coefficients k_{ij} are the renormalized kinetic coefficients. The mode-coupling calculation yields*

$$K_{ij} = K_{ij}^0 + \alpha_i \alpha_j S \quad (108)$$

*The coefficients K_{ij} in Ref. 30 correspond to $n^{-1} K_{ij}$ in this paper.

where K_{ij}^0 is the background part, α_1 and $\alpha_2 = \alpha_c X(1-X)$ are defined by (50)-(52) and are plotted in Fig. 1, and

$$S = (k_B T / 6\pi\eta\xi) R \quad (109)$$

Here η is the shear viscosity, R is defined by (55) and behaves as (94) on the critical isochore, and ξ is the thermal correlation length. Therefore, $S \propto \xi^{\gamma/\nu-1} \approx \xi$, since $\gamma \approx 2\nu$. See Appendix D. The above result is equivalent to that of Mistura.¹⁸ Anisimov *et al.*²⁴ obtained the result

$$\lim_{T \rightarrow T_c} K_{11} / K_{12} = \lim_{T \rightarrow T_c} K_{12} / K_{22} = -k_B (dT/d\Delta)_c$$

which is apparently wrong. Note that (107) can be used only when the characteristic wave number of the process is less than ξ^{-1} .

3.2. Collective Modes and Rayleigh Scattering

Two diffusive modes are obtained from (107). It will be shown that one mode undergoes critical showing-down, with its diffusion constant D_1 of order ξ^{-1} , whereas the other mode exhibits no critical slowing-down, with its diffusion constant D_2 nearly nonsingular. D_1 can be measured by dynamic light scattering.¹⁶

To proceed further from (107), the 2×2 matrix $\mathbf{A} = \{A_{ij}\}$ is given by

$$A_{ij} = A_{ji} = (\partial h_i / \partial m_j)_p \quad (110)$$

where m_i and h_j are defined by (105) and (106), and the derivative in (110) is performed with the pressure and the other density (m_1 or m_2) held fixed. In the usual notation A_{ij} are given by

$$A_{11} = \frac{k_B}{T} \left(\frac{\partial T}{\partial s} \right)_{pX}, \quad A_{12} = \frac{1}{T} \left(\frac{\partial \Delta}{\partial s} \right)_{pX} = \frac{1}{T} \left(\frac{\partial T}{\partial X} \right)_{ps}, \quad A_{22} = \frac{1}{k_B T} \left(\frac{\partial \Delta}{\partial X} \right)_{ps} \quad (111)$$

Then (107) is written in the following vector equation:

$$\frac{\partial}{\partial t} \mathbf{m} = \nabla^2 \mathbf{H} \cdot \mathbf{m} \quad (112)$$

where

$$\mathbf{H} = \mathbf{K} \cdot \mathbf{A} \quad (113)$$

The two eigenvalues of \mathbf{H} are D_1 and D_2 :

$$\mathbf{H} \cdot \mathbf{e}_j = D_j \mathbf{e}_j \quad (114)$$

where $j = 1, 2$ and the \mathbf{e}_j are the corresponding eigenvectors.

Denote the inverse matrix of \mathbf{A} by $\mathbf{B} = \{b_{ij}\}$. Then, $b_{ij} = b_{ji} = (\partial m_i / \partial h_j)$, where the derivative is performed with the other fields held fixed. Namely,

$$b_{11} = \frac{T}{k_B} \left(\frac{\partial S}{\partial T} \right)_{p\Delta}, \quad b_{12} = T \left(\frac{\partial S}{\partial \Delta} \right)_{pT} = T \left(\frac{\partial X}{\partial T} \right)_{p\Delta}, \quad b_{22} = k_B T \left(\frac{\partial X}{\partial \Delta} \right)_{pT} \quad (115)$$

From (54) the most singular part of b_{ij} is $\alpha_i \alpha_j R$, so that b_{ij} is divided into two parts as

$$b_{ij} = b_{ij}^0 + R \alpha_i \alpha_j \quad \text{or} \quad \mathbf{B} = \mathbf{B}^0 + R \boldsymbol{\alpha} \boldsymbol{\alpha} \quad (116)$$

where $\mathbf{B}^0 = \{b_{ij}^0\}$. The first term b_{ij}^0 consists of the background part and the weakly divergent part. Hereafter the product of two vectors \mathbf{a} and \mathbf{b} , \mathbf{ab} , denotes the matrix with components $a_i b_j$. The inverse of \mathbf{B} , \mathbf{A} , is then of the form

$$a_{ij} = a_{ij}^0 - P \beta_i \beta_j \quad \text{or} \quad \mathbf{A} = \mathbf{A}^0 - P \boldsymbol{\beta} \boldsymbol{\beta} \quad (117)$$

where

$$\mathbf{A}^0 = \{a_{ij}^0\} = (\mathbf{B}^0)^{-1} \quad (118)$$

$$\boldsymbol{\beta} = \mathbf{A}^0 \cdot \boldsymbol{\alpha} \quad \text{or} \quad \boldsymbol{\alpha} = \mathbf{B}^0 \cdot \boldsymbol{\beta} \quad (119)$$

$$P = R / [1 + R(\boldsymbol{\alpha} \cdot \boldsymbol{\beta})] \approx 1 / (\boldsymbol{\alpha} \cdot \boldsymbol{\beta}) \quad (120)$$

Now using (108) and (117), one can express \mathbf{H} , (113), as

$$\mathbf{H} = \mathbf{H} \cdot (\mathbf{I} - P \boldsymbol{\alpha} \boldsymbol{\beta}) + \frac{S}{1 + R(\boldsymbol{\alpha} \cdot \boldsymbol{\beta})} \boldsymbol{\alpha} \boldsymbol{\beta} \quad (121)$$

where

$$\mathbf{H}^0 = \mathbf{K}^0 \cdot \mathbf{A}^0 \quad (122)$$

and $\mathbf{I} = \{\delta_{ij}\}$ is the unit matrix. Because $S \propto \xi$ and $R \propto \xi^2$ and the inner product $\boldsymbol{\alpha} \cdot \boldsymbol{\beta}$ is of order one (even in the pure fluid limit), \mathbf{H} can be approximated as

$$\mathbf{H} \approx \mathbf{H}^0 \cdot \left(\mathbf{I} - \frac{1}{\boldsymbol{\alpha} \cdot \boldsymbol{\beta}} \boldsymbol{\alpha} \boldsymbol{\beta} \right) + \frac{S}{R} \frac{1}{\boldsymbol{\alpha} \cdot \boldsymbol{\beta}} \boldsymbol{\alpha} \boldsymbol{\beta} \quad (123)$$

where the terms of order ξ^{-2} have been neglected. The first term vanishes when it operates on $\boldsymbol{\alpha}$, and the second term remains as

$$\mathbf{H} \cdot \boldsymbol{\alpha} = (S/R) \boldsymbol{\alpha} + O(\xi^{-2}) \quad (124)$$

Therefore, $\mathbf{e}_1 \approx \boldsymbol{\alpha}$ and $D_1 \approx S/R$. More precisely, retaining the term of order ξ^{-2} , one obtains

$$D_1 = k_B T / 6\pi\eta\xi + S_0 / R + O(\xi^{-3}) \quad (124)$$

where

$$S_0 = [K_{11}^0 K_{22}^0 - (K_{12}^0)^2] / (\alpha_1^2 K_{22}^0 + \alpha_2^2 K_{11}^0 - 2\alpha_1 \alpha_2 K_{12}^0) \quad (126)$$

In the dilute limit, $D_1 \approx K_{11}/b_{11}$.

On the other hand, because

$$D_1 + D_2 = \text{Tr } H = \sum_{j=1}^2 H_{jj}$$

the diffusion constant D_2 is nearly nonsingular as

$$\begin{aligned} D_2 &\approx \text{Tr } \mathbf{H}^0 - \frac{1}{\boldsymbol{\alpha} \cdot \boldsymbol{\beta}} (\boldsymbol{\beta} \cdot \mathbf{H}^0 \cdot \boldsymbol{\alpha}) \\ &\approx (\alpha_1^2 K_{22}^0 + \alpha_2^2 K_{11}^0 - 2\alpha_1 \alpha_2 K_{12}^0) / (\alpha_1^2 b_{22}^0 + \alpha_2^2 b_{11}^0 - 2\alpha_1 \alpha_2 b_{12}^0) \end{aligned} \quad (127)$$

The second line of (127) can be derived by explicitly calculating the coefficients of K_{ij}^0 . The denominator of (127) contains a weakly divergent part, but it is negligibly small compared to the regular part for $|t| \geq t_{s2}$. The expression for D_2 seems somewhat complicated. However, because $|\alpha_1| \gg |\alpha_2|$ in the nearly azeotropic case, one can set $\alpha_2 = 0$ in (127) to a good approximation to obtain

$$D_2 \approx K_{22}^0 / b_{22}^0 + \dots \quad (128)$$

The error is negligible in any fluid, particularly in the case $X \rightarrow 0$ or 1, because α_2 , K_{12}^0 , K_{22}^0 , b_{12}^0 , and b_{22}^0 are proportional to $X(1-X)$, whereas α_1 , K_{11}^0 , and b_{11}^0 are nonvanishing even if $X(1-X) \rightarrow 0$. Namely, the terms neglected in (128) are of higher order with respect to the factor $X(1-X)$.

With the above results it is now possible to calculate the time correlation functions of the dynamic variables $\hat{m}_1 = (\hat{s} - s)/k_B$ and $\hat{m}_2 = \hat{X} - X$, where \hat{s} and \hat{X} are defined by (21) and (22) and s and X are the equilibrium values. In Appendix D for $k\xi \ll 1$ it is found that

$$\begin{aligned} G_{ij}(k, t) &= n \int d\mathbf{r} \langle \hat{m}_i(\mathbf{r}, t) \hat{m}_j(\mathbf{0}, 0) \rangle \exp(-i\mathbf{k} \cdot \mathbf{r}) \\ &= (R\alpha_i \alpha_j + C_{ij}^{(1)}) \exp(-D_1 k^2 t) \\ &\quad + C_{ij}^{(2)} \exp(-D_2 k^2 t) \end{aligned} \quad (129)$$

where the coefficients $C_{ij}^{(1)}$ and $C_{ij}^{(2)}$ are nearly nonsingular. Obviously, in the kinetic region $k\xi \geq 1$, one should replace R and $D_1 k^2$ by $R/(1+k^2 \xi^2)$ and Γ_k , respectively, where $\Gamma_k \approx D_1 k^2$ for $k\xi \leq 1$ and $\Gamma_k \approx (k_B T / 16\eta) k^3$ for $k\xi \geq 1$. Therefore, the generalization of (128) is

$$G_{ij}(k, t) = \left(\frac{R\alpha_i \alpha_j}{1+k^2 \xi^2} + C_{ij}^{(1)} \right) e^{-\Gamma_k t} + C_{ij}^{(2)} e^{-D_2 k^2 t} \quad (130)$$

In the dynamic light scattering in ${}^3\text{He}$ - ${}^4\text{He}$ the measurable correlation function is that of the number density $\hat{n} = \hat{n}_3 + \hat{n}_4$. This is because the electric polarizabilities of ${}^3\text{He}$ and ${}^4\text{He}$ molecules are nearly the same. In the presence of deviations δT and $\delta\Delta$, the nonequilibrium deviation δn can be written as

$$\delta n \approx \left(\frac{\partial n}{\partial T} \right)_{p\Delta} dT + \left(\frac{\partial n}{\partial \Delta} \right)_{pT} \delta\Delta \approx nR \left(\alpha_1 \frac{\delta T}{T} + \alpha_2 \frac{\delta\Delta}{k_B T} \right) \quad (131)$$

where use has been made of (25) and (54). Therefore, δn is related to m_j by

$$\delta n \approx nR\alpha \cdot \mathbf{h} \approx nR\alpha \cdot \mathbf{A} \cdot \mathbf{m} \approx n(\alpha \cdot \beta)^{-1} \beta \cdot \mathbf{m} \quad (132)$$

Thus, insofar as the Brillouin scattering is neglected, the density variable $\delta\hat{n}$ can be replaced by the variable $n(\alpha \cdot \beta)^{-1} \beta \cdot \hat{\mathbf{m}}$ in the correlation function. Therefore, the time-correlation function of the density $I(k, t)$ is given by

$$\begin{aligned} I(k, t) &\equiv n^{-1} \int d\mathbf{r} [(\hat{n}(\mathbf{r}, t) - n)[\hat{n}(\mathbf{0}, 0) - n]] \exp(-i\mathbf{k} \cdot \mathbf{r}) \\ &\approx R[\exp(-\Gamma_k t)] / (1 + k^2 \xi^2) + C_r \exp(-D_2 k^2 t) \end{aligned} \quad (133)$$

The coefficient C_r is nearly nonsingular and the second term can be neglected as $T \rightarrow T_c$. There are no essential differences in the Rayleigh scattering between the pure fluid case and the mixture case. This is in agreement with the data of Miura *et al.*¹⁶

3.3. Transport Coefficients

3.3.1. Isothermal Diffusion Constant D

Consider first the isothermal diffusion constant D . By setting $\nabla T = 0$ and $\nabla\Delta = (\partial\Delta/\partial X)_{pT} \nabla X$, one finds $(\partial/\partial t)X = D\nabla^2 X$, with

$$D = \frac{1}{k_B T} K_{22} \left(\frac{\partial\Delta}{\partial X} \right)_{pT} \approx \frac{K_{22}^0 + \alpha_2^2 S}{C_0 X(1-X) + \alpha_2^2 R} \quad (134)$$

Here the weakly divergent term in (93) has been neglected. The background value of the diffusion constant is thus given by

$$D_0 = K_{22}^0 / C_0 X(1-X) = K_{22}^0 / b_{22}^0 \quad (135)$$

where b_{22}^0 is defined by (116). From (128) it can be seen that

$$D_0 \approx D_2 + \dots \quad (136)$$

The error becomes small as $\alpha_2 \rightarrow 0$ and is of higher order in $X(1-X)$. The quantity D_0 will not vary considerably along the critical line. When $X \approx 1$

(or 0), D_0 tends to the diffusion constant of an isolated ^4He (or ^3He) molecule in ^3He (or ^4He). One anticipates $D_0 \approx 10^{-4}$ cm²/sec from light scattering experiments near the λ line³³ and near the liquid-vapor critical line.¹⁶

In terms of D_0 and α_c (90), D can be rewritten as

$$D \approx \frac{D_0 + (\alpha_c^2/C_0)X(1-X)S}{1 + (\alpha_c^2/C_0)X(1-X)R} \quad (137)$$

Now a dynamic crossover reduced temperature t_D is found by equating the two terms in the numerator of (137). Because $\xi = \xi_0 t^{-\nu}$ and $R = R_0 t^{-\gamma}$ with $t = T/T_c - 1$ on the critical isochore, one obtains

$$t_D^{\gamma-\nu} = (k_B T / 6\pi\eta\xi_0 D_0) A_0 X(1-X) = (k_B T / 6\pi\eta\xi_0 D_0) t_{s1}^{\gamma} \quad (138)$$

where A_0 and t_{s1} are defined by (95) and (99), respectively, and use has been made of (109). Here $k_B T / 6\pi\eta\xi_0 \approx 0.5 \times 10^{-4}$ cm²/sec along the critical line in ^3He - ^4He .¹⁴ Thus, in ^3He - ^4He ,

$$t_D^{\nu} \approx 10^{-1} X(1-X) \quad \text{and} \quad t_D \approx t_{s1}^2 \quad (139)$$

Therefore, D behaves on the critical isochore as

$$\bar{D} \approx \begin{cases} D_0/[1 + A_0 X(1-X)t^{-\gamma}] & \text{for } t \geq t_D \\ k_B T / 6\pi\eta\xi & \text{for } t \leq t_D \end{cases} \quad (140a)$$

$$\quad \quad \quad (140b)$$

Miura *et al.* calculated D at $X = 0.79$ from data of the Rayleigh linewidth and the thermodynamic derivatives. Table I compares their estimated values and the theoretical expression (137). Agreement is fair in view of the considerable uncertainty of D . The result suggests $D_0 \approx 0.5 \times 10^{-4}$ cm²/sec.

TABLE I

The Calculated Diffusion Constant D^{16} and the Product $D[1 + A_0 X(1-X)t^{-\gamma}]$ on the Critical Isochore at $X = 0.79^a$

t	$D \times 10^5$, cm ² /sec	$1 + A_0 X(1-X)t^{-\gamma}$	$D[1 + A_0 X(1-X)t^{-\gamma}] \times 10^4$, cm ² /sec	$\delta D/D$
10^{-2}	1.93	3.39	0.64	0.38
7×10^{-3}	1.38	4.62	0.64	0.38
4×10^{-3}	0.82	7.93	0.65	0.40
2×10^{-3}	0.28	16.47	0.46	0.26
10^{-3}	0.13	35.58	0.46	0.24

^aHere $A_0 = 0.069$ from Fig. 2, so that $t_{s1} = 2 \times 10^{-2}$ and $t_D = 4 \times 10^{-4}$. The above product should be equal to $D_0[1 + (t_D/t)^{\gamma-\nu}]$ from (137). In the observed temperature region it should be nearly equal to the background diffusion constant D_0 , and one finds $D_0 \approx 0.5 \times 10^{-4}$ cm²/sec. However, it tends to decrease as $t \rightarrow 0$, contrary to the theory. I do not consider this discrepancy as crucial, because of the large estimated uncertainty, $\pm \delta D/D$.

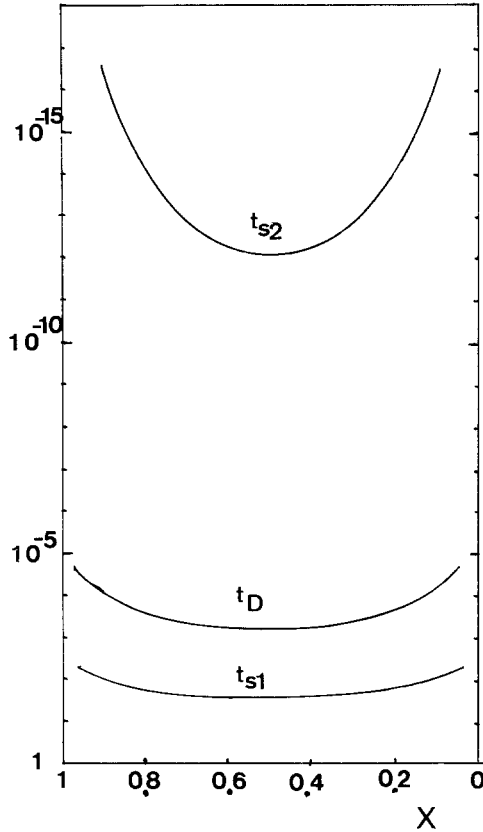


Fig. 6. The three crossover reduced temperatures t_{s1} , t_{s2} , and t_D as functions of X in ${}^3\text{He}-{}^4\text{He}$. Here $t_{s1} = [0.06X(1-X)]^{1/\gamma}$, $t_{s2} = [0.25X(1-X)]^{1/\alpha}$, and $t_D = t_{s1}^2$, with $\gamma = 1.16$ and $\alpha = 0.1$.

For ${}^3\text{He}-{}^4\text{He}$ the three crossover reduced temperatures t_{s1} , t_{s2} , and t_D are displayed in Fig. 6. They satisfy

$$t_{s2} \ll t_D \ll t_{s1} \quad (141)$$

3.3.2. Thermal Conductivity κ

The heat flow experiment is always performed in the absence of the ${}^3\text{He}$ mass flux. Then, from (107) for $i = 2$, we have in the final stationary state

$$K_{12}\nabla h_1 + K_{22}\nabla h_2 = 0 \quad (142)$$

One can eliminate h_2 from the first equation of (107) ($i = 1$) to obtain³⁰

$$\kappa = k_B n (K_{11} - K_{12}^2 / K_{22}) \quad (143)$$

Substitution of (108) yields

$$\kappa = \frac{k_B n [K_{11}^0 K_{22}^0 - (K_{12}^0)^2] + (\alpha_1^2 K_{22}^0 + \alpha_2^2 K_{11}^0 - 2\alpha_1 \alpha_2 K_{12}^0) S}{K_{22}^0 + \alpha_2^2 S} \quad (144)$$

As $S \rightarrow \infty$, κ ultimately approaches a very large limit κ_c given by

$$\kappa_c = k_B n (K_{22}^0 \alpha_1^2 / \alpha_2^2 + K_{11}^0 - 2K_{12}^0 \alpha_1 / \alpha_2) \quad (145)$$

In the nearly azeotropic case or the dilute case, one obtains an approximation for κ_c

$$\kappa_c \approx k_B n K_{22}^0 \alpha_1^2 / \alpha_2^2 \approx (\alpha_1^2 C_0 / \alpha_c^2) k_B n D_0 / X(1 - X) \quad (146)$$

where use has been made of (90) and (135).

For pure ^3He (or ^4He), $\kappa_c = \infty$, and

$$\kappa / k_B n = (k_B T / 6\pi\eta\xi) \alpha_1^2 R + K_{11}^0 \quad (147)$$

Here

$$(k_B T / 6\pi\eta\xi) \alpha_1^2 R = 5.2 \times 10^{-5} t^{-\gamma+\nu} \text{ cm}^2/\text{sec}$$

on the critical isochore.^{14,23} Equation (147) is consistent with the result of Ref. 23,

$$\kappa / k_B n = (3.7t^{-0.57} + 130) \times 10^{-5} \text{ cm}^2/\text{sec}$$

in ^3He . This suggests that the background value of κ ,

$$\kappa_{\text{reg}} = k_B n [K_{11}^0 - (K_{12}^0)^2 / K_{22}^0] \quad (148)$$

is of order $1.3 \times 10^{-3} k_B n$ along the critical line. The measurements at $X = 0.66$ and 0.8 surely show that κ_{reg} is only weakly dependent on X .^{14,15} Then,

$$\kappa_c / \kappa_{\text{reg}} \approx 10^2 / X(1 - X) \gg 1 \quad (149)$$

The saturation of κ to κ_c can be attained only for $\alpha_2^2 S \geq K_{22}^0$ or for $|t| \leq t_D$ on the critical isochore. It is convenient to express κ in the form

$$\kappa = \kappa_s \kappa_c / (\kappa_s + \kappa_c) \quad \text{or} \quad 1/\kappa = 1/\kappa_c + 1/\kappa_s \quad (150)$$

The κ_s grows strongly and is of the form

$$\kappa_s = k_B n b_c^2 (S + S_0) \quad (151)$$

where S_0 is defined by (126) and

$$b_c = (\alpha_1^2 K_{22}^0 + \alpha_2^2 K_{11}^0 - 2\alpha_1 \alpha_2 K_{12}^0) / (\alpha_1 K_{22}^0 - \alpha_2 K_{12}^0) \quad (152)$$

If $|\alpha| \ll 1$, one can set $\alpha_2 = 0$ in (152) to give $b_c \approx \alpha_1$ and

$$\kappa_s \approx k_B n \alpha_1^2 S + \kappa_{\text{reg}} \quad (153)$$

where κ_{reg} is defined by (148). Therefore, if $|\alpha_2|$ is small, one obtains on the critical isochore

$$\kappa_s / \kappa_c = \alpha_2^2 S / K_{22}^0 \approx (t_D / t)^{\gamma - \nu} \quad (154)$$

$$\kappa \approx \kappa_s / [1 + (t_D / t)^{\gamma - \nu}] \quad (155)$$

3.3.3. Thermodiffusion Ratio k_T

The thermodiffusion ratio is defined by the following ratio in a steady state with a constant heat flow:

$$k_T = -T \nabla c / \nabla T \quad (156)$$

Here c is the mass concentration and is related to the molar concentration X by $c = M_3 X / [M_3 X + M_4(1 - X)]$, where M_3 and M_4 are the ^3He and ^4He masses. Hence

$$k_T = -(M_3 M_4 / \bar{M}^2) T \nabla X / \nabla T \quad (157)$$

where $\bar{M} = M_3 X + M_4(1 - X)$ is the average mass.

Equation (141) can be rewritten into a relation between ∇X and ∇T .

$$K_{12} \frac{\nabla T}{T} + K_{22} \left[\left(\frac{\partial \Delta}{\partial X} \right)_{pT} \frac{\nabla X}{k_B T} + \left(\frac{\partial \Delta}{\partial T} \right)_{p\Delta} \frac{\nabla T}{k_B T} \right] = 0 \quad (158)$$

Therefore, use of

$$(\partial \Delta / \partial T)_{p\Delta} = -(\partial X / \partial T) / (\partial X / \partial \Delta)_{pT}$$

gives

$$k_T = -\frac{M_3 M_4}{\bar{M}^2} \left[k_B \left(\frac{\partial X}{\partial T} \right)_{p\Delta} - k_B \left(\frac{\partial X}{\partial \Delta} \right)_{pT} \frac{K_{12}}{K_{22}} \right] \quad (159)$$

The quantity in the brackets is expressed as $b_{12} - b_{22} K_{12} / K_{22}$ from (115). Substitution of (108) and (116) yields

$$\begin{aligned} k_T = & -\frac{M_3 M_4}{\bar{M}^2} \left[\left(b_{12}^0 - b_{22}^0 \frac{K_{12}^0}{K_{22}^0} \right) - \alpha_2 \left(\alpha_1 - \alpha_2 \frac{b_{12}^0}{b_{22}^0} \right) \frac{S}{D_0} \right. \\ & \left. + \alpha_2 \left(\alpha_1 - \alpha_2 \frac{K_{12}^0}{K_{22}^0} \right) R \right] \left(1 + \alpha_2^2 \frac{S}{K_{22}^0} \right)^{-1} \end{aligned} \quad (160)$$

Far from the criticality k_T is given by the background part $k_{T,\text{reg}}$, which is of the form

$$k_{T,\text{reg}} = -\frac{M_3 M_4}{\bar{M}^2} \left(\frac{b_{12}^0}{b_{22}^0} - \frac{K_{12}^0}{K_{22}^0} \right) C_0 X(1-X) \quad (161)$$

where b_{22}^0 has been replaced by $C_0 X(1-X)$. Experimentally, it is known that $k_{T,\text{reg}} = -0.08X(1-X)$,³⁴ so that the coefficient in front of $X(1-X)$ in (161) would be a small number, of the order of 0.08.

As $T \rightarrow T_c$, the second term in the numerator of (160) is of order $-\alpha_2 t^{-(\gamma-\nu)}$ and the third term of order $\alpha_2 t^{-\gamma}$. Furthermore, the background part appears to be of order $10^{-1}X(1-X)$, so that the third term is dominant for $|t| \ll 1$ and

$$k_T \approx -\frac{M_3 M_4}{\bar{M}^2} \alpha_1 \alpha_2 \left(1 - \frac{\alpha_2 K_{12}^0}{\alpha_1 K_{22}^0} \right) R \left(1 + \frac{\alpha_2^2 S}{K_{22}^0} \right)^{-1} \quad (162)$$

On the critical isochore k_T behaves as

$$k_T = -A_T X(1-X) t^{-\gamma} / [1 + (t_D/t)^{\gamma-\nu}] \quad (163)$$

where

$$A_T = (M_3 M_4 / \bar{M}^2) \alpha_1 \alpha_c R_0 (1 - \alpha_2 K_{12}^0 / \alpha_1 K_{22}^0) \quad (164)$$

For $1 \gg t \geq t_D$ one has the relation

$$k_T \approx -T(\partial c / \partial T)_{p\Delta} (1 - \alpha_2 K_{12}^0 / \alpha_1 K_{22}^0) \quad (165)$$

Here²⁹

$$(\partial c / \partial T)_{p\Delta} = (M_3 M_4 / \bar{M}^2) (\partial X / \partial T)_{p\Delta}$$

Therefore $k_T \propto t^{-\gamma}$ for $t \geq t_D$, in agreement with experiment.^{14,15} At present it is not possible to estimate the value of K_{12}^0 / K_{22}^0 . However, it is very plausible that $|\alpha_2 K_{12}^0 / \alpha_1 K_{22}^0|$ is considerably smaller than one at any X . See discussions below (169). Then $A_T \approx 0.2$. Experimentally,^{14,15} $k_T \approx -0.024 t^{-\gamma}$ both at $X = 0.66$ and 0.8 , which implies $A_T = 0.11$ and 0.15 at $X = 0.66$ and 0.8 , respectively. On the other hand, (164) together with Figs. 1 and 2 indicate $A_T = 0.23$ and 0.25 at $X = 0.66$ and 0.8 , respectively, if the factor $\alpha_2 K_{12}^0 / \alpha_1 K_{22}^0$ is neglected. I consider this agreement as fair, because the Duke group calculated k_T from data of the density gradient and did not measure the concentration gradient directly.

The Duke group measured the dielectric constant gradient, which is proportional to the density gradient ∇n in ^3He - ^4He mixtures. In the present scheme it is of the form

$$\frac{\nabla n}{\nabla T} = \left(\frac{\partial n}{\partial T} \right)_{p\Delta} - k_B \left(\frac{\partial n}{\partial \Delta} \right)_{pT} \frac{K_{12}}{K_{22}} \quad (166)$$

From (25) and (54) one can set

$$\left(\frac{\partial n}{\partial T}\right)_{p\Delta} = \frac{n}{T}(b_{31}^0 + \alpha_1 R), \quad k_B \left(\frac{\partial n}{\partial \Delta}\right)_{pT} = \frac{n}{T}(b_{32}^0 + \alpha_2 R) \quad (167)$$

where b_{31}^0 and b_{32}^0 are nearly nonsingular. Then

$$\frac{\nabla n}{\nabla T} \approx \frac{n}{T} \alpha_1 \frac{(1 - \alpha_2 K_{12}^0 / \alpha_1 K_{22}^0) R}{1 + \alpha_2^2 S / K_{22}^0} \quad (168)$$

where the terms nonsingular or of order S have been neglected in the numerator. Thus $\nabla n / \nabla T$ is negative and grows as $t^{-\gamma}$ for $t \geq t_D$, in accord with the data. For $1 \gg t \geq t_D$ the following relation holds:

$$\nabla n / \nabla T \approx (1 - \alpha_2 K_{12}^0 / \alpha_1 K_{22}^0) (\partial n / \partial T)_{p\Delta} \quad (169)$$

This relation can be used to estimate $\alpha_2 K_{12}^0 / \alpha_1 K_{22}^0$ or K_{12}^0 / K_{22}^0 if the ratio $(\nabla n / \nabla T) / (\partial n / \partial T)_{p\Delta}$ is precisely determined. From the data at $X = 0.8$ it is possible to say only that $|\alpha_2 K_{12}^0 / \alpha_1 K_{22}^0|$ is much smaller than one.^{14,15} From the data at $X = 0.66$, $\alpha_2 K_{12}^0 / \alpha_1 K_{22}^0 \approx 0.3$ or $K_{12}^0 / K_{22}^0 \approx 4$. However, it is not possible to decide whether this estimation is reliable or not.

Finally, I give a simple explanation of the results. If $|\alpha_2 K_{12}^0 / \alpha_1 K_{22}^0| \ll 1$, then $\nabla c / \nabla T \approx (\partial c / \partial T)_{p\Delta}$ and $\nabla n / \nabla T \approx (\partial n / \partial T)_{p\Delta}$ for $t \geq t_D$ from (165) and (169). That is, the variation of Δ is negligible compared to that of T in calculating the variations of the density variables. From (25), (45), and (54) this surely holds if $|\alpha_2 \delta \Delta| \ll k_B |\alpha_1 \delta T|$. In the steady state without diffusion flux (142) holds and one is led to the following criterion:

$$|\alpha_2 \delta \Delta / k_B \alpha_1 \delta T| \approx |\alpha_2 K_{12}^0 / \alpha_1 K_{22}^0| \ll 1 \quad (170)$$

Using (108) and (138), it can be shown that $\alpha_2 K_{12}^0 / \alpha_1 K_{22}^0$ is of order $(t_D / t)^{\gamma - \nu}$ for $t \geq t_D$ and tends to one for $|t| \ll t_D$. Thus (170) is valid for $t \geq t_D$. In other words, as long as the background thermodiffusion is small, the thermodiffusion effect is apparently nonexistent for $t \geq t_D$ (namely, $K_{12} = 0$). This is in accord with the interpretation given in Ref. 14.

4. SUMMARY

The main results of this paper can be summarized as follows:

1. In Section 2 the variances of the energy density $\hat{\epsilon}$ and the number densities \hat{n}_j are related to the second derivatives of $\omega = p / k_B T$ with respect to $B = 1 / k_B T$ and $\nu_j = \mu_j / k_B T$. Next the entropy variable \hat{s} and the concentration variable \hat{X} were introduced. The variances of \hat{s} , \hat{X} , and the number density $\hat{n} = \hat{n}_3 + \hat{n}_4$ are related to the second derivatives of μ_4 with respect to T , $\Delta = \mu_3 - \mu_4$, and p . Using these relations and the postulates of

Griffiths and Wheeler, it has been possible to express the singularities of various thermodynamic derivatives in terms of parameters representing the geometry of CXS. Depending on these parameters, there can be various crossover phenomena on approaching the critical line.

In this paper I have been mainly interested in the nearly azeotropic case $|\alpha_2| \ll 1$, where α_2 is defined by (1) and is a parameter representing how the Δ axis is orthogonal to the normal to the coexistence surface. If $|\alpha_2| \ll 1$, the concentration susceptibility $(\partial X / \partial \Delta)_{pT}$ begins to grow strongly only for $|T/T_c - 1| \lesssim t_{s1}$, where t_{s1} is defined by (3) or (99). The transport coefficients cross over for $|T/T_c - 1| \approx t_D \approx t_{s1}^2$, where t_D is defined by (5) or (138). The ^3He - ^4He system is nearly azeotropic. Furthermore, in ^3He - ^4He the critical temperature and the critical pressure depend on the concentration rather weakly and the following relation holds: $(dp/dT)_c \approx (dp/dT)_{\Delta, \text{CXS}}$ [see (10), (84), and (104)]. Then, the crossover associated with the weak singularity is characterized by a single crossover reduced temperature t_{s2} , where t_{s2} is defined by (9) or (101). Here, $t_{s2} \ll t_D \ll t_{s1}$.

2. The singular parts of the kinetic coefficient K_{ij} are given by $\alpha_i \alpha_j S$ with S strongly divergent. This has been shown on the basis of a simple mode-coupling calculation. The divergent parts are expected to be of this form even within a higher order approximation. Also in ^3He - ^4He near the superfluid transition the singular parts of K_{ij} can be shown generally to be of the form $g_{i0} g_{j0} S$, where g_{i0} are constants and S diverges as $T \rightarrow T_\lambda$.³⁰ These relations imply that the thermal conductivity κ without ^3He mass flux is of the form $\kappa = \kappa_c \kappa_s / (\kappa_c + \kappa_s)$, where κ_c tends to a constant and κ_s diverges strongly on approaching criticality.³⁵ The saturation of κ was observed near the λ point, but has not been observed near the plait point.

APPENDIX A

Consider a local equilibrium distribution defined by^{27,29}

$$\rho_{\text{local}} = N^{-1} \exp \left\{ - \int d\mathbf{r} \frac{1}{k_B T(\mathbf{r})} [\hat{\epsilon}(\mathbf{r}) - \mu_3(\mathbf{r}) \hat{n}_3(\mathbf{r}) - \mu_4(\mathbf{r}) \hat{n}_4(\mathbf{r})] \right\} \quad (\text{A1})$$

Here $T(\mathbf{r}) = T + \delta T(\mathbf{r})$, $\mu_3(\mathbf{r}) = \mu_3 + \delta \mu_3(\mathbf{r})$, and $\mu_4(\mathbf{r}) = \mu_4 + \delta \mu_4(\mathbf{r})$ are the local temperature and the local chemical potentials. The deviations $\delta T(\mathbf{r})$, $\delta \mu_3(\mathbf{r})$, and $\delta \mu_4(\mathbf{r})$ are assumed to be infinitesimal and vary very slowly in space. The N in (A1) is the normalization constant. Then expanding ρ_{local} with respect to the deviations yields

$$\rho_{\text{local}} = \rho_{\text{eq}} \left\{ 1 + \int d\mathbf{r} [\delta \hat{\Omega}(\mathbf{r}) - \langle \delta \hat{\Omega}(\mathbf{r}) \rangle] \right\} \quad (\text{A2})$$

Here ρ_{eq} is the equilibrium distribution and

$$\delta\hat{\Omega}(\mathbf{r}) = -\hat{\varepsilon}(\mathbf{r}) \delta B(\mathbf{r}) + \hat{n}_3(\mathbf{r}) \delta\nu_3(\mathbf{r}) + \hat{n}_4(\mathbf{r}) \delta\nu_4(\mathbf{r}) \quad (\text{A3})$$

where $\delta B = -\delta T/k_B T^2$ and $\delta\nu_j = \delta\mu_j/k_B T - \mu_j \delta T/k_B T^2$.

Let $\hat{A}(\mathbf{r})$ be any local variable. Then the average of $\hat{A}(\mathbf{r})$ over ρ_{local} is given by

$$\langle \hat{A}(\mathbf{r}) \rangle_{\text{local}} = \langle \hat{A}(\mathbf{r}) \rangle + \int d\mathbf{r}' \langle [\hat{A}(\mathbf{r}) - \langle \hat{A}(\mathbf{r}) \rangle] \delta\hat{\Omega}(\mathbf{r}') \rangle \quad (\text{A4})$$

where $\langle \cdots \rangle_{\text{local}}$ and $\langle \cdots \rangle$ are the averages over ρ_{local} and ρ_{eq} , respectively. Here $A \equiv \langle \hat{A}(\mathbf{r}) \rangle$ is regarded as a function of B , ν_3 , and ν_4 . In the limit of slow variation of the deviations, δA is given by

$$\delta A = \frac{\partial A}{\partial B} \delta B + \frac{\partial A}{\partial \nu_3} \delta \nu_3 + \frac{\partial A}{\partial \nu_4} \delta \nu_4 \quad (\text{A5})$$

This leads to the relations

$$\partial A / \partial B = -\langle \hat{A} : \hat{\varepsilon} \rangle, \quad \partial A / \partial \nu_j = \langle \hat{A} : \hat{n}_j \rangle \quad (\text{A6})$$

By setting $\hat{A} = \hat{\varepsilon}$ or \hat{n}_j , one readily obtains (14)–(16) using (17).

The pressure deviation $\delta p(\mathbf{r})$ and the chemical potential difference deviation $\delta\Delta(\mathbf{r})$ can be expressed as

$$\delta p(\mathbf{r}) = ns \delta T(\mathbf{r}) + n_3 \delta\mu_3(\mathbf{r}) + n_4 \delta\mu_4(\mathbf{r}) \quad (\text{A7})$$

$$\delta\Delta(\mathbf{r}) = \delta\mu_3(\mathbf{r}) - \delta\mu_4(\mathbf{r}) \quad (\text{A8})$$

Then one finds

$$\delta\hat{\Omega}(\mathbf{r}) = \hat{s}(\mathbf{r}) \frac{n \delta T(\mathbf{r})}{k_B T} + \hat{X}(\mathbf{r}) \frac{n \delta\Delta(\mathbf{r})}{k_B T} + \hat{n}(\mathbf{r}) \frac{\delta p(\mathbf{r})}{nk_B T} + \text{const} \quad (\text{A9})$$

where the variables \hat{s} and \hat{X} are defined by (21) and (22). Now regarding $A = \langle \hat{A}(\mathbf{r}) \rangle$ as a function of p , T , and Δ , one obtains

$$\frac{\partial A}{\partial T} = \frac{n}{k_B T} \langle \hat{s} : \hat{A} \rangle, \quad \frac{\partial A}{\partial \Delta} = \frac{n}{k_B T} \langle \hat{X} : \hat{A} \rangle, \quad \frac{\partial A}{\partial p} = \frac{1}{nk_B T} \langle \hat{n} : \hat{A} \rangle \quad (\text{A10})$$

From (21) and (22),

$$\delta \langle s \rangle = \langle \hat{s} \rangle_{\text{local}} - \langle \hat{s} \rangle = \frac{1}{nT} (\delta u - Ts \delta n - \mu_3 \delta n_3 - \mu_4 \delta n_4) = \delta s \quad (\text{A11})$$

$$\delta \langle X \rangle = \langle \hat{X} \rangle_{\text{local}} - \langle \hat{X} \rangle = \frac{1}{n} [(1-X) \delta n_3 - X \delta n_4] = \delta X \quad (\text{A12})$$

In (A11) use has been made of the thermodynamic relation $du = Td(nS) + \mu_3 dn_3 + \mu_4 dn_4$, while in (A12) use has been made of (25). Therefore, the deviations of the averages of the variables \hat{s} and \hat{X} , $\delta\langle\hat{s}\rangle$ and $\delta\langle\hat{X}\rangle$, are surely equal to the deviations of the thermodynamic quantities s and X . By setting $\hat{A} = \hat{s}$, \hat{X} , and \hat{n} , one obtains (25).

APPENDIX B

Leung and Griffiths (LG) introduced the following field variables:

$$\zeta = C_4 e^{\nu_4}/\Theta, \quad \tau = B_c(\zeta) - B, \quad h = \ln \Theta - H(\zeta, \tau) \quad (\text{B1})$$

where

$$\Theta = C_3 e^{\nu_3} + C_4 e^{\nu_4} \quad (\text{B2})$$

with C_3 and C_4 being positive constants. $B_c(\zeta)$ is the critical value of B and $H(\zeta, \tau)$ is the value of $\ln \Theta$ on CXS. The potential ω consists of a regular part $\omega_r = c(\zeta) + d(\zeta)\tau + f(\zeta)h$ and a singular part $\omega_s = q(\zeta)\pi(\bar{\tau}, h)$, where $\bar{\tau} = l(\zeta)\tau$ and π is approximated to be the potential pB calculated from the Schofield linear model. The functions of ζ , c , d , f , q , and l are polynomials of ζ . Furthermore, $B_c = a_0 + a_1\zeta$ and $H = b_1\zeta + b_2\zeta^2 + g_1\zeta\tau$.

First note the relations

$$\frac{\partial}{\partial B} = H_\tau \frac{\partial}{\partial h} - \frac{\partial}{\partial \tau} \quad (\text{B3})$$

$$\frac{\partial}{\partial \nu_3} + \frac{\partial}{\partial \nu_4} = \frac{\partial}{\partial h} \quad (\text{B4})$$

where $H_\tau = \partial H/\partial \tau = g_1\zeta$. The partial derivatives on the left-hand sides of (B3) and (B4) are to be taken with B , ν_3 , and ν_4 as independent variables, whereas those on the right-hand sides are with h , τ , and ζ as independent variables. Then,

$$\begin{aligned} n = \frac{\partial \omega}{\partial h}, \quad \langle \hat{n} : \hat{n} \rangle &= \frac{\partial^2 \omega}{\partial h^2}, \quad \langle \hat{\varepsilon} : \hat{\varepsilon} \rangle = \left(H_\tau \frac{\partial}{\partial h} - \frac{\partial}{\partial \tau} \right)^2 \omega \\ \langle \hat{n} : \hat{\varepsilon} \rangle &= - \left(H_\tau \frac{\partial}{\partial h} - \frac{\partial}{\partial \tau} \right) \frac{\partial \omega}{\partial h} \end{aligned} \quad (\text{B5})$$

The n here is denoted ρ by LG. These relations lead to

$$U = B^2 \left[\frac{\partial^2 \omega}{\partial \tau^2} - \left(\frac{\partial^2 \omega}{\partial h \partial \tau} \right)^2 \left(\frac{\partial^2 \omega}{\partial h^2} \right)^{-1} \right] \left(\frac{\partial \omega}{\partial h} \right)^{-1} \quad (\text{B6})$$

where $G_{ij}(k, t)$ is defined by the first line of (129).

Next consider the derivative $(\partial/\partial\Delta)_{pT}$. If p and T are fixed, it follows that $d\omega = n_3 d\nu_3 + n_4 d\nu_4 = 0$, $d\nu_3 = (1-X)B d\Delta$, and $\delta\nu_4 = -XB d\Delta$. Further using

$$(\partial\tau/\partial\nu_3)_{B,\nu_4} = -(\partial\tau/\partial\nu_4)_{B,\nu_3} = -\zeta(1-\zeta)a_1 \quad (\text{B7})$$

$$(\partial\zeta/\partial\nu_3)_{B,\nu_4} = -(\partial\zeta/\partial\nu_4)_{B,\nu_3} = -\zeta(1-\zeta) \quad (\text{B8})$$

one obtains

$$B^{-1}\left(\frac{\partial}{\partial\Delta}\right)_{pT} = \alpha_2 \frac{\partial}{\partial h} - \zeta(1-\zeta)\left(a_1 \frac{\partial}{\partial\tau} + \frac{\partial}{\partial\zeta}\right) \quad (\text{B9})$$

Here α_2 is defined by (51) and $a_1 = dB_c/d\zeta$. One can calculate $B^{-1}(\partial X/\partial\zeta)_{pT}$ if use is made of the relation

$$X = \left(\frac{\partial\omega}{\partial\omega_3}\right) / n = \frac{\partial h}{\partial\nu_3} + \frac{\partial\tau}{\partial\nu_3} \frac{\partial\omega}{\partial\tau} / \frac{\partial\omega}{\partial h} + \frac{\partial\zeta}{\partial\nu_3} \frac{\partial\omega}{\partial\zeta} / \frac{\partial\omega}{\partial h} \quad (\text{B10})$$

The equivalent calculation was performed by LG. The result is given by $(1-\zeta)G/\rho$, where G is defined by (2.32) of LG. Thus one obtains (93).

The coefficient β_3 in (61) can be calculated from

$$\begin{aligned} n(\hat{n}_3; \hat{\varepsilon}) &= -\frac{\partial^2\omega}{\partial\nu_3 \partial B} \\ &= \left(\frac{\partial h}{\partial\nu_3} \frac{\partial}{\partial h} + \frac{\partial\tau}{\partial\nu_3} \frac{\partial}{\partial\tau} + \frac{\partial\zeta}{\partial\nu_3} \frac{\partial}{\partial\zeta}\right) \left(-H_\tau \frac{\partial}{\partial h} + \frac{\partial}{\partial\tau}\right) \omega \end{aligned} \quad (\text{B11})$$

On the right-hand side, the coefficient in front of $\partial^2\omega/\partial\tau^2$ should be equal to $B\beta_3$ from (61) and (B6), so that

$$\beta_3 = \beta_2 = B^{-1} \partial\tau/\partial\nu_3 = -\zeta(1-\zeta)a_1 B^{-1} \quad (\text{B12})$$

This is equivalent to (89). Then one can calculate β_∞ (91), numerically.

LG calculated the determinant $E \equiv \partial(u, \rho, x)/\partial(\tau, \zeta, h)$ in (2.30) of LG. Det Ω in our notation is equal to E multiplied by

$$\rho^{-1} \partial(h, \tau, \zeta)/\partial(B, \nu_3, \nu_4) = \rho^{-1} \zeta(1-\zeta)$$

Retaining the most singular terms gives (102) with

$$C_1 = \left[-\frac{\partial^2 H}{\partial\zeta^2} + \left(\frac{\partial^2 C}{\partial\zeta^2}\right) f^{-1} \right] \frac{\zeta^1(1-\zeta)^2}{X^2(1-X)^2} \quad (\text{B13})$$

APPENDIX C

Griffiths and Wheeler's theory implies

$$\lim_{T \rightarrow T_c} \left(\frac{\partial T}{\partial \Delta} \right)_{sn} = \left(\frac{dT}{d\Delta} \right)_c \quad (C1)$$

which is a special application of Eq. (4.13a) of Ref. 7. Next note the relation

$$\left(\frac{\partial T}{\partial \Delta} \right)_{sn} = \frac{H^{12}}{H^{22}} = \frac{H_{13}H_{23} - H_{33}H_{12}}{H_{11}H_{33} - H_{13}^2} \quad (C2)$$

where H^{ij} and H_{ij} are defined by (40) and (41). From (25) one can express $(\partial T/\partial \Delta)_{sn}$ in terms of the variances as

$$\left(\frac{\partial T}{\partial \Delta} \right)_{sn} = \frac{\langle \hat{n} : \hat{s} \rangle \langle \hat{n} : \hat{X} \rangle - \langle \hat{n} : \hat{n} \rangle \langle \hat{s} : \hat{X} \rangle}{\langle \hat{s} : \hat{s} \rangle \langle \hat{n} : \hat{n} \rangle - \langle \hat{s} : \hat{n} \rangle^2} \quad (C3)$$

Use of (71)–(75) yields

$$(\partial T/\partial \Delta)_{sn} = -(\beta_2 U + \dots)/(\beta_1 U + \dots) \quad (C4)$$

where terms finite as $T \rightarrow T_c$ are not written explicitly. Thus,

$$\beta_2 \approx -\beta_1 \left(\frac{dT}{d\Delta} \right)_c \approx - \left(1 - \frac{\Delta_c}{k_B T_c} \beta_2 \right) \left(\frac{dT}{d\Delta} \right)_c \quad (C5)$$

where use has been made of (69). Equation (C5) is solved to give (70).

APPENDIX D

The enhancement of the kinetic coefficients arises from the nonlinear coupling between m_i and the transverse part of the velocity field $\mathbf{v}(\mathbf{r}, t)$, where $\nabla \cdot \mathbf{v} = 0$. The mode-coupling approximation yields the fluctuation contribution in the form

$$\Delta K_{ij} \approx n \int_0^\infty dt \int d\mathbf{r} \langle \hat{m}_i(\mathbf{r}, t) \hat{v}_x(\mathbf{r}, t) \hat{m}_j(\mathbf{0}, 0) \hat{v}_x(\mathbf{0}, 0) \rangle \quad (D1)$$

where the carets denote that the quantities in $\langle \dots \rangle$ are the dynamic variables. Use of the decoupling approximation makes it possible to transform (D1) as

$$\Delta K_{ij} = (k_B T / 3\pi^2 \rho) \int_0^\infty dt \int_0^\infty dk k^2 e^{-(\eta k^2 t / \rho)} G_{ij}(k, t) \quad (D2)$$

where $G_{ij}(k, t)$ is defined by the first line of (129).

I anticipate the form (129) for $G_{ij}(k, t)$ and pick up the singular term proportional to R . Then (108) can be derived. Note that (129) is derived on the basis of (108), so that the derivation of (108) is self-consistent. To derive (108) more completely one can construct a self-consistent matrix equation for K_{ij} from (D2) not assuming (108). However, the final result is nothing but (108).

APPENDIX E

Here (129) is derived. First I introduce vectors $\bar{\mathbf{e}}_j$ by

$$\bar{\mathbf{e}}_j = \mathbf{A} \cdot \mathbf{e}_j \quad (\text{E1})$$

From (114) they satisfy

$$(\mathbf{H})^T \cdot \bar{\mathbf{e}}_j = D_j \bar{\mathbf{e}}_j$$

where $(\mathbf{H})^T = \mathbf{A} \cdot \mathbf{K}$ is the transposed matrix of \mathbf{H} . One can readily show $\bar{\mathbf{e}}_i \cdot \mathbf{e}_j \propto \delta_{ij}$, so that any vector \mathbf{a} can be decomposed as $\mathbf{a} = \sum_{j=1}^2 \mathcal{P}_j \cdot \mathbf{a}$, where \mathcal{P}_j is the following projection matrix:

$$\mathcal{P}_j = (\bar{\mathbf{e}}_j \cdot \mathbf{e}_j)^{-1} \bar{\mathbf{e}}_j \mathbf{e}_j \quad (\text{E2})$$

The matrix $\mathbf{G}(k, t)$, (129), is then of the form

$$\mathbf{G}(k, t) = \sum_{j=1}^2 e^{-iD_j k^2} \mathcal{P}_j \cdot \mathbf{B} \quad (\text{E3})$$

where use has been made of (115). Since $\mathbf{B} \cdot \bar{\mathbf{e}}_j = \mathbf{e}_j$, one has

$$\mathbf{G}(k, t) = \sum_{j=1}^2 e^{-iD_j k^2} (\bar{\mathbf{e}}_j \cdot \mathbf{e}_j)^{-1} \bar{\mathbf{e}}_j \mathbf{e}_j \quad (\text{E4})$$

Next express \mathbf{e}_j as follows:

$$\mathbf{e}_1 = \boldsymbol{\alpha} + f_1 \boldsymbol{\beta}_\perp, \quad \mathbf{e}_2 = \boldsymbol{\beta}_\perp + f_2 \boldsymbol{\alpha} \quad (\text{E5})$$

I have defined

$$\boldsymbol{\beta}_\perp = \begin{pmatrix} -\beta_2 \\ \beta_1 \end{pmatrix}, \quad \boldsymbol{\alpha}_\perp = \begin{pmatrix} -\alpha_2 \\ \alpha_1 \end{pmatrix} \quad (\text{E6})$$

so that $\boldsymbol{\beta}_\perp \cdot \boldsymbol{\beta} = \boldsymbol{\alpha}_\perp \cdot \boldsymbol{\alpha} = 0$. From the relation $\boldsymbol{\beta} \cdot \mathbf{H} \cdot \mathbf{e}_1 = D_1(\boldsymbol{\alpha} \cdot \boldsymbol{\beta})$ one finds

$$f_1(\boldsymbol{\beta} \cdot \mathbf{H}_0 \cdot \boldsymbol{\beta}_\perp) = \left[D_1 - \frac{S}{1 + R(\boldsymbol{\alpha} \cdot \boldsymbol{\beta})} \right] (\boldsymbol{\alpha} \cdot \boldsymbol{\beta}) + [1 + R(\boldsymbol{\alpha} \cdot \boldsymbol{\beta})]^{-1} (\boldsymbol{\beta} \cdot \mathbf{H}^0 \cdot \boldsymbol{\alpha}) \quad (\text{E7})$$

Therefore $f_1 \propto 1/R$. The vector $\bar{\mathbf{e}}_1$ is of the form

$$\bar{\mathbf{e}}_1 = [1 + R(\boldsymbol{\alpha} \cdot \boldsymbol{\beta})]^{-1} \boldsymbol{\beta} + f_1 \mathbf{A}_0 \cdot \boldsymbol{\beta}_\perp \quad (\text{E8})$$

Noting the relation $\mathbf{A}_0 \cdot \boldsymbol{\beta}_\perp = (\text{Det } \mathbf{B}^0)^{-1} \boldsymbol{\alpha}_\perp$, one has

$$\bar{\mathbf{e}}_1 \cdot \mathbf{e}_1 = R^{-1} + O(R^{-2}) \quad (\text{E9})$$

On the other hand, \mathbf{e}_2 becomes independent of $T - T_c$ as $T \rightarrow T_c$ and

$$f_2 \approx (\boldsymbol{\beta} \cdot \mathbf{H}^0 \cdot \boldsymbol{\beta}_\perp) / (\boldsymbol{\alpha} \cdot \boldsymbol{\beta}) D_2 \quad (\text{E10})$$

Using (E5), (E9), and (E10), one can arrive at (129).

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