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Tricritical dynamics of multicomponent fluids

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Abstract. Tricritical anomalies of transport coefficients of diffusive type in multicomponent fluids are studied theoretically for the thermodynamic model system due to Griffiths. Transport anomalies are characterized by the two critical modes whose decay rates behave as ξ^{-3} , ξ being the range of correlation of critical fluctuations. Usefulness of the variables having a diagonal susceptibility matrix considered by Tisza as well as by Gunton and Green in the present problem is indicated.

1. Introduction

In the last years higher-order critical points in multicomponent fluids whose possibility was first pointed out by Kohnstamm in 1926 have been receiving increasing attention, notably by Widom and Griffiths (Widom 1973, Griffiths and Widom 1973, Griffiths 1974). The important merit of dealing with these systems lies in the fact that the field conjugate to the order parameter can be actually controlled. At a time when much is understood for equilibrium tricritical behaviour and various tricritical systems are identified (Griffiths 1973, and references quoted therein), it is timely to start looking into the dynamical behaviour of these systems where, so far, liquid ^3He - ^4He mixture (Kawasaki and Gunton 1972, Grover and Swift 1973) and certain metamagnetic systems (Huber 1974) have been treated.

The present paper is concerned with a study of dynamical behaviour near tricritical points of multicomponent fluids where we shall limit our discussion to transport phenomena of vectorial character, namely, diffusion and heat conduction. Recently Griffiths (1974) constructed a thermodynamic model of multicomponent fluids of sufficiently general character, and this model will be our starting point in the following. After describing the equilibrium tricritical behaviour on the basis of the Griffiths model in § 2 we will discuss non-equilibrium behaviour in § 3 with some simplifying assumptions, the validity of which will be examined in § 4.

2. Equilibrium tricritical behaviour

Here, the Griffiths thermodynamic model with some necessary modifications and extensions is briefly described to the extent needed in this work. We assume a one-dimensional order parameter ψ and construct the singular part of an appropriate free energy Φ as

$$\Phi = g_1\psi + g_2\psi^2 + g_3\psi^3 + g_4\psi^4 + \psi^6. \quad (2.1)$$

The actual value of ψ is determined by minimizing Φ with respect to ψ and the free energy is thus obtained as a function of the 'fields' g_1, g_2, g_3 and g_4 , which we denote again as $\Phi(g_1, g_2, g_3, g_4)$. Griffiths notes that Φ has the following scaling property:

$$\Phi(l^{\varphi_1}g_1, l^{\varphi_2}g_2, l^{\varphi_3}g_3, l^{\varphi_4}g_4) = l\Phi(g_1, g_2, g_3, g_4) \tag{2.2}$$

with†

$$\varphi_1 = \frac{5}{6}, \quad \varphi_2 = \frac{2}{3}, \quad \varphi_3 = \frac{1}{2}, \quad \varphi_4 = \frac{1}{3}. \tag{2.3}$$

As far as the thermodynamic model is concerned, it is not necessary, however, that the exponents φ_i take the particular values (2.3) but it is sufficient to assume

$$1 > \varphi_1 > \varphi_2 > \varphi_3 > \varphi_4 > 0. \tag{2.4}$$

For symmetrical tricritical points g_1 is the field conjugate to the order parameter, g_2 measures the distance from the λ and triple line whereas g_4 is the distance from the tricritical point measured parallel to this line, and g_3 is zero. In this case the crossover exponent ϕ is given by

$$\phi = \varphi_2/\varphi_4. \tag{2.5}$$

Very near the λ line (that is, the line of normal critical points) at a finite distance from the tricritical point g_3 and g_4 remain finite in general and $\Phi(g_1, g_2)$ satisfies the scaling property near the normal critical point:

$$\Phi(l^{\psi_1}g_1, l^{\psi_2}g_2) = l\Phi(g_1, g_2) \tag{2.6}$$

where, using the conventional notation for normal critical exponents, we have

$$\psi_1 = (d + 2 - \eta)/2d, \quad \psi_2 = 1/vd, \tag{2.7}$$

d being the dimensionality of space.

The free energy which satisfies both (2.2) and (2.6) and hence is valid in the crossover region as well takes the following functional form:

$$\Phi = g_2^{1/\psi_2} g_4^{(1/\varphi_4)(1 - \varphi_2/\psi_2)} \Phi^* \left(\frac{g_1}{g_2^{\psi_1/\psi_2} g_4^{(1/\varphi_4)(\varphi_1 - \psi_1\varphi_2/\psi_2)}}, \frac{g_3}{g_2^{\varphi_3/\varphi_2}}, \frac{g_4}{g_2^{\varphi_4/\varphi_2}} \right). \tag{2.8}$$

The scaling behaviour near the tricritical point described here and below has been discussed by a number of authors including Riedel (1972), Hankey *et al* (1972) and Griffiths (1973).

We define the density variables m_i in the sense of Griffiths and Wheeler (1970) which are conjugate to g_i as follows:

$$m_i = - \frac{\partial \Phi}{\partial g_i}. \tag{2.9}$$

In the original Griffiths model (2.1), $m_j = \psi^j$ but this will not be used in this work. We

† These exponents also arise naturally in the renormalization group treatment of tricritical points due to Riedel and Wegner (1972). Their scaling fields $\mu_{k,l}$ are related to the fields g_i by $g_{2k+l} = \mu_{k,l} + \text{constant}$ where $k = 0, 1, 2, \dots$ and $l = 0, 1$. The eigenvalues of the renormalization transformation associated with the 'eigenvector' $\mu_{k,l}$ is $2^{y_{k,l}}$ with $y_{k,l} = 3 - (k + \frac{1}{2}l)$. The exponents $y_{k,l}$ of the relevant eigenvectors are $y_{0,1} = \frac{5}{2}$, $y_{1,0} = 2$, $y_{1,1} = \frac{3}{2}$ and $y_{2,0} = 1$, since $\mu_{0,0}$ is a constant and $\mu_{2,1}$ can be eliminated by suitably adjusting an additive constant to the order parameter. Hence in the expression for g_{2k+l} given above only the first term is important from the renormalization group point of view and $\frac{1}{3}y_{kl} = \varphi_{2k+l}$.

will need the wavenumber-dependent susceptibility matrix $\chi_{ij}(\mathbf{k})$ with $i, j = 1, 2, 3, 4$ defined by

$$\chi_{ij}(\mathbf{k}) = \frac{1}{V} \langle m_i(\mathbf{k}) m_j(-\mathbf{k}) \rangle \tag{2.10}$$

where $m_i(\mathbf{k})$ is the Fourier component of fluctuation $\delta m_i(\mathbf{r})$ of the local values of m_i given by

$$m_i(\mathbf{k}) = \int e^{-i\mathbf{k} \cdot \mathbf{r}} \delta m_i(\mathbf{r}) d\mathbf{r} \tag{2.11}$$

and an angular bracket denotes the equilibrium average and V is the system volume. We assume that fluctuations of the density variables are characterized by a single length ξ which has the following scaling form corresponding to (2.8):

$$\xi = g_2^{-\nu} g_4^{(\varphi_2/\varphi_4)(\nu-\nu_1)} \xi^* \tag{2.12}$$

where ξ^* is a function of the three variables contained in Φ^* of (2.8) and ν_1 is the equivalent of ν in the tricritical region and is equal to $\frac{1}{2}$ for (2.1).

Apart from some scaling functions, the singular parts of $\chi_{ij}(\mathbf{k})$ behave as follows. In the tricritical region,

$$\chi_{ij}(\mathbf{k}) \sim k^{-\gamma_{ij}^\dagger/\nu_1} + (\text{a regular part}) \tag{2.13}$$

and near the λ line[†],

$$\chi_{ij}(\mathbf{k}) \sim k^{-\gamma_{ij}^\ddagger/\nu} \quad (i, j = 1, 2) \tag{2.14}$$

with

$$\gamma_{ij}^\dagger \equiv (\varphi_i + \varphi_j - 1)/\varphi_2 \tag{2.15}$$

$$\gamma_{ij}^\ddagger = (\psi_i + \psi_j - 1)/\psi_2, \quad (i, j = 1, 2). \tag{2.16}$$

The values of γ_{ij}^\dagger for (2.3) as well as the expressions of γ_{ij} in terms of the usual notation are summarized in tables (1a and b).

Combining (2.13) and (2.14) the form of $\chi_{ij}(\mathbf{k})$ valid in the crossover region as well can be written down as follows. For $i, j = 1, 2$

$$\chi_{ij}(\mathbf{k}) = k^{-\gamma_{ij}/\nu} g_4^{(\varphi_2/\varphi_4)[(\nu/\nu_1)\gamma_{ij} - \gamma_{ij}^\dagger]} \chi_{ij}^* + (\text{a regular part}), \tag{2.17}$$

Table 1. (a) Critical exponents γ_{ij}^\dagger and (b) critical exponents γ_{ij}

(a)					(b)		
1	2	3	4	<i>i</i> / <i>j</i>	1	2	<i>i</i> / <i>j</i>
1	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	1	γ	$(\alpha + \gamma)/2$	1
	$\frac{1}{2}$	$\frac{1}{4}$	0	2		α	2
		0	$-\frac{1}{4}$	3			
			$-\frac{1}{2}$	4			

[†] The notations such as γ_{ij} were also employed by Fisher (1973) in generalizing the scaling law ideas recently.

and for $i = 3, 4$ and $j = 1, 2, 3, 4$ and in the tricritical region,

$$\chi_{ij}(\mathbf{k}) = k^{-\gamma_{ij}^*} \chi_{ij}^* + (\text{a regular part}) \tag{2.18}$$

where χ_{ij}^* is a function of $k\zeta$ and the three variables contained in Φ^* of (2.8). (2.18) reflects the fact that the variables m_3 and m_4 no longer exhibit critical fluctuations on the λ line.

We now go on to discuss a few more points needed subsequently.

First we will need the relationship between the scaling variables (m_i, g_i) and the physical variables (a_i, h_i) where the physical field h_i is related to g_i through

$$h_i = \sum_{j=1}^4 B_{ij} g_j + h_{i1} \tag{2.19}$$

where h_{i1} is the value of h_i at the tricritical point, and in contrast to the case treated by Griffiths (1974) we allow for more than four physical field variables. Inverting (2.19) with $i = 1, 2, 3, 4$ we have

$$g_i = g_i(h_1 - h_{11}, h_2 - h_{21}, h_3 - h_{31}, h_4 - h_{41}). \tag{2.20}$$

If there are more than four field variables, the tricritical 'line' is represented parametrically by the equation

$$h_i = h_{i1}(h_5, h_6, \dots), \quad i = 1, 2, 3, 4. \tag{2.21}$$

The singular parts of the physical density variables again denoted as a_i are defined by

$$a_i = -\partial\Phi/\partial h_i \quad \text{for all } i. \tag{2.22}$$

Or, for $i = 1, 2, 3, 4$

$$a_i = -\sum_{j=1}^4 \frac{\partial\Phi}{\partial g_j} \frac{\partial g_j}{\partial h_i} = \sum_{j=1}^4 m_j \frac{\partial g_j}{\partial h_i} \tag{2.23}$$

and for $i = 5, 6, \dots$

$$a_i = \sum_{j=1}^4 \frac{\partial\Phi}{\partial g_j} \sum_{l=1}^4 \frac{\partial g_j}{\partial h_l} \frac{\partial h_{l1}}{\partial h_i} = -\sum_{j=1}^4 \sum_{l=1}^4 m_j \frac{\partial g_j}{\partial h_l} \frac{\partial h_{l1}}{\partial h_i}. \tag{2.24}$$

Both can now be written as

$$a_i = \sum_{j=1}^4 C_{ij} m_j \quad \text{for all } i \tag{2.25}$$

with the coefficients C_{ij} defined by (2.23) and (2.24).

The second point is concerned with alternative choices of the variables (g_i, m_i) . Griffiths (1974) has shown that the singular properties and the phase diagram of his thermodynamic model (2.1) and its generalized version satisfying (2.2) and (2.4) remain unchanged under the following affine transformation†

$$g'_i = \sum_j D_{ij} g_j, \quad m'_i = \sum_j (D^{-1})_{ji} m_j \tag{2.26}$$

with $D_{ii} = 1$ and $D_{ij} = 0$ for $i < j$, consequently, $(D^{-1})_{ji} = 0$ for $i > j$. A special transformation of this type is Tisza's restricted unimodular transformation which diagonalizes the matrix $\chi_{ij}(\mathbf{k})$ (Tisza 1966). This transformation was used recently by Gunton and

† Griffiths is concerned only near the tricritical point but the statement evidently applies near the λ line for the first two variables provided $\psi_1 > \psi_2$.

Green (1971) to construct a hierarchy of nested subspaces of the density variables, each of which is characterized by a set of in general degenerate (ie equally singular) diagonal elements of the susceptibility matrix $\chi(\mathbf{k})$. We suppose that such a transformation has been carried out for our density variables as well as the spatial Fourier components $m_i(\mathbf{k})$ thereof. We then obtain a set of new variables m'_i or $m'_i(\mathbf{k})$ and the new susceptibility matrix $\chi'(\mathbf{k})$ which again behaves as (2.13), (2.14) or (2.17), (2.18) with, of course, no off-diagonal elements.

3. Non-equilibrium tricritical behaviour

Let us consider an $N + 1$ component fluid with chemical potentials $\mu_0, \mu_1, \dots, \mu_N$ where the zeroth component is the solvent. $N + 2$ field variables $h_0, h_1, h_2, \dots, h_{N+1}$, can be chosen to be

$$\begin{aligned} h_i &= \mu_i/M_i - \mu_0/M_0, & i &= 1, 2, \dots, N \\ h_0 &= T, h_{N+1} = -p \end{aligned} \quad (3.1)$$

where M_i is the molecular mass of the i th component and T and p are the temperature and the pressure, respectively. Choice of μ_0/M_0 as the free energy Φ allows us to introduce the density variables through

$$d(\mu_0/M_0) = v dp - s dT - \sum_{i=1}^N c_i dh_i \quad (3.2)$$

where v and s are the specific volume and the specific entropy, respectively, and c_i is the mass fraction of the i th component. Since we are concerned with transport phenomena of vectorial character, we shall drop pressure hereafter.

The linearized hydrodynamic equation describing vectorial transport is

$$\rho T \frac{\partial s}{\partial t} = -\nabla \cdot (\mathbf{q} - \sum_{i=1}^N h_i \mathbf{i}_i) \quad (3.3)$$

$$\rho \frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{i}_i, \quad i = 1, 2, \dots, N \quad (3.4)$$

where \mathbf{q} is the heat current and \mathbf{i}_i is the diffusion current of the i th component, and

$$\mathbf{i}_i = - \sum_{j=1}^N \alpha_{ij} \nabla h_j - \beta_i \nabla T \quad (3.5)$$

$$\mathbf{q} = - \sum_{i=1}^N \beta_i T \nabla h_i - \gamma \nabla T + \sum_{i=1}^N h_i \mathbf{i}_i \quad (3.6)$$

where we adopted the notation of Landau and Lifshitz (1959) for the Onsager kinetic coefficients α, β and γ in generalized form. The correlation function expressions for the Onsager kinetic coefficients are (see, for instance, Mistura 1972)

$$\alpha_{ij} = \frac{1}{k_B T} \int d\mathbf{r} \int_0^\infty dt \langle I_i^\alpha(\mathbf{r}, t) I_j^\alpha(0, 0) \rangle \quad (3.7)$$

$$\beta_i = \frac{1}{k_B T^2} \int d\mathbf{r} \int_0^\infty dt \langle I_i^\alpha(\mathbf{r}, t) I_s^\alpha(0, 0) \rangle \quad (3.8)$$

$$\gamma = \frac{1}{k_B T^2} \int d\mathbf{r} \int_0^\infty dt \langle I_s^x(\mathbf{r}, t) I_s^x(0, 0) \rangle \quad (3.9)$$

where I_i^x and I_s^x are the molecular expressions for i_i^x and $q^x - \sum_{i=1}^N h_i i_i^x$, respectively.

In what follows we find it convenient to cast the foregoing in a more symmetrical form by introducing the $N + 1$ component currents j_0, j_1, \dots, j_N by

$$j_0 \equiv \left(\mathbf{q} - \sum_{i=1}^N h_i \mathbf{i}_i \right) / \rho T, \quad j_i = \mathbf{i}_i / \rho, \quad (i = 1, 2, \dots, N) \quad (3.10)$$

and the $N + 1$ density variables a_0, a_1, \dots, a_N by

$$a_0 = s, \quad a_i = c_i, \quad (i = 1, 2, \dots, N). \quad (3.11)$$

The linearized hydrodynamic equation takes the following simple form:

$$\frac{\partial a_i}{\partial t} = -\mathbf{V} \cdot \mathbf{j}_i \quad (i = 0, 1, \dots, N) \quad (3.12)$$

$$\mathbf{j}_i = - \sum_{j=0}^N L_{ij} \nabla h_j \quad (i = 0, 1, \dots, N) \quad (3.13)$$

where the new Onsager kinetic coefficients L_{ij} are,

$$L_{00} = \gamma / \rho T, \quad L_{0i} = L_{i0} = \beta_i / \rho, \quad L_{ij} = \alpha_{ij} / \rho \quad (i, j = 1, 2, \dots, N) \quad (3.14)$$

and the correlation function expression for L_{ij} is

$$L_{ij} = \frac{\rho}{k_B T} \int_0^\infty dt \int d\mathbf{r} \langle J_i^x(\mathbf{r}, t) J_j^x(0, 0) \rangle \quad (3.15)$$

where J_i^x is the molecular expression for j_i^x .

We now study the tricritical anomalies of (3.15) in the simplest mode-coupling approximation (Kawasaki 1974) where the current density becomes

$$J_i^x(\mathbf{r}, t) = u^x(\mathbf{r}, t) \delta a_i(\mathbf{r}, t) \quad (3.16)$$

where u^x is the x component of the local velocity and δa_i is the fluctuation of the density variable a_i . Here we present a simple-minded treatment and the problems in this treatment will be discussed in the next section. We assume that the shear viscosity does not exhibit a strong critical anomaly (see the next section). Then, any critical divergence of L_{ij} arises from strong critical anomalies of the equal-time correlations $\langle \delta a_i(\mathbf{r}) \delta a_j(0) \rangle$. This allows us to substitute (2.25) into (3.16). If we can assume that the time variation of (3.16) is dominated by the viscous relaxation of u^x (see the next section), we have for the singular contribution to (3.15) which is again denoted as L_{ij} ,

$$L_{ij} = \sum_{l=1}^4 \sum_{n=1}^4 C_{il} C_{jn} \bar{L}_{ln} \quad (3.17)$$

where \bar{L}_{ij} is obtained as

$$\bar{L}_{ij} \equiv \frac{1}{(2\pi)^3} \int d\mathbf{k} \frac{2}{3\nu^* k^2} \chi_{ij}(\mathbf{k}). \quad (3.18)$$

Here ν^* is the kinetic viscosity η / ρ and $\chi_{ij}(\mathbf{k})$ is given by (2.10).

Substituting the behaviour (2.13) and (2.14) into (3.18), the singular contributions to \bar{L}_{ij} arising from fluctuations with wavenumbers of the order of ξ^{-1} behave as follows. In the tricritical region,

$$\bar{L}_{ij} \sim \xi^{\zeta_{ij}^1/\nu_t} \tag{3.19}$$

and near the λ line

$$\bar{L}_{ij} \sim \xi^{\zeta_{ij}^2/\nu} \quad (i, j = 1, 2) \tag{3.20}$$

with

$$\zeta_{ij}^1 \equiv \text{greater of } \gamma_{ij}^1 - \nu_t \text{ and } -\nu_t \tag{3.21}$$

$$\zeta_{ij}^2 \equiv \gamma_{ij} - \nu \quad (i, j = 1, 2). \tag{3.22}$$

The values of these exponents which correspond to table 1 are now summarized in table 2. We thus find that in the tricritical region only \bar{L}_{11} and \bar{L}_{12} exhibit clear divergence and \bar{L}_{22} and \bar{L}_{13} are either finite or at most weakly divergent for the model system (2.1). Near the λ line, only \bar{L}_{11} diverges strongly and any divergence of \bar{L}_{12} will be characterized by a small exponent, which is already known (Swift 1968, Kawasaki 1974).

Table 2. (a) critical exponents ζ_{ij}^1 and (b) critical exponents ζ_{ij}^2

(a)					(b)		
1	2	3	4	$i \backslash j$	1	2	$i \backslash j$
$\frac{1}{2}$	$\frac{1}{4}$	0	$-\frac{1}{4}$	1	$\gamma - \nu$	$\frac{x + \gamma}{2} - \nu$	1
	0	$-\frac{1}{4}$	$-\frac{1}{2}$	2		$x - \nu$	2
		$-\frac{1}{2}$	$-\frac{1}{2}$	3			
			$-\frac{1}{2}$	4			

Combining (3.19) and (3.20) and noting (3.12) we can write down a general scaling form for \bar{L}_{ij} (the singular part only) with $i, j = 1$ and 2 valid in the crossover region as well as follows:

$$\bar{L}_{ij} = g_2^{-\zeta_{ij}} g_4^{(\varphi_2/\varphi_4)(\zeta_{ij} - \zeta_{ij}^1)} \bar{L}_{ij}^* \tag{3.23}$$

where \bar{L}_{ij}^* is again a function of the variables contained in Φ^* of (2.8).

We conclude this section with two remarks. In Rayleigh scattering experiments we will need wavenumber- and frequency-dependent kinetic coefficients $\bar{L}_{ij}(q, \omega)$. Since the viscous damping dominates the intermediate states, the frequency dependence can be ignored. $\bar{L}_{ij}(q)$ is then obtained from (3.18) by replacing $\chi_{ij}(\mathbf{k})$ by $\chi_{ij}(\mathbf{q} - \mathbf{k})$. The scaling behaviour of \bar{L}_{ij} is again given by (3.23) where now \bar{L}_{ij}^* also depends upon $q\xi$.

If we use the transformed variables $m_i(\mathbf{k})$ discussed at the end of § 2, the transformed Onsager kinetic coefficient matrix $\bar{L}'_{ij}(q)$ becomes diagonal provided the coefficients D_{ij} are non-singular and hence their dependence on wavenumbers can be ignored†. Here

† Gunton and Green (1971) argue that these coefficients are indeed finite at the critical point. Alternatively, we may suppose that the variables m_i are chosen at the outset in such a way that the matrix $\chi(\mathbf{k})$ is diagonal.

the variables $m'_i(\mathbf{k})$ need not be restricted to the four singular variables near the tricritical point but can be supplemented with non-singular variables so as to cover the entire $N + 1$ diffusive modes. The linearized macroscopic law equivalent to (3.3) ~ (3.6) takes a simple form in terms of the new density variables,

$$n_i(\mathbf{k}) \equiv m'_i(\mathbf{k})/[\chi_{ii}(\mathbf{k})]^{1/2} \tag{3.24}$$

as

$$\frac{\partial}{\partial t} n_i(\mathbf{k}, t) = - \sum_j \Gamma_{ij}(\mathbf{k}) n_j(\mathbf{k}, t) \tag{3.25}$$

with

$$\Gamma_{ij}(\mathbf{k}) = k^2(k_B T/\rho)[\bar{L}_{ij}(k) + L_{ij}^0(k)]/[\chi_{ii}(\mathbf{k})\chi_{jj}(\mathbf{k})]^{1/2} \tag{3.26}$$

where $L_{ij}^0(k)$ is the finite regular part of the Onsager kinetic coefficient. We now limit our consideration to the tricritical region and we will find

$$\Gamma_{ij}(k) \sim \zeta^{\sigma_{ij}} \tag{3.27}$$

where the values of the exponents σ_{ij} are obtained from (2.13), (3.19) and tables 1(a and b), and the tricritical behaviour of $\Gamma_{ij}(k)$ for the model (2.1) is represented symbolically as

$$\zeta^2 \cdot \Gamma_{ij}(k) \sim \begin{pmatrix} \zeta^{-1} & \zeta^{-1} & \zeta^{-1} & \zeta^{-1} & \dots \\ \zeta^{-1} & \zeta^{-1} & \zeta^{-1/2} & \zeta^{-1/2} & \dots \\ \zeta^{-1} & \zeta^{-1/2} & \zeta^0 & \zeta^0 & \dots \\ \zeta^{-1} & \zeta^{-1/2} & \zeta^0 & \zeta^0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix} \tag{3.28}$$

where dots merely denote repetition of the respective matrix elements that precede them. From this we see that, barring accidental cancellations of terms, the two smallest eigenvalues of $\Gamma(k)$ behave as ζ^{-3} in the tricritical region, and the rest as ζ^0 . This ‘degeneracy’ of the first two relaxation rates is understood if we note that for diverging \bar{L}_{ij} including the cases where $\zeta_{ij}^1 = 0$

$$\sigma_{ij} = -2 - \frac{\gamma_{ii}^1 + \gamma_{jj}^1}{2\nu_i} + \frac{\zeta_{ij}^1}{\nu_i} = -3. \tag{3.29}$$

4. Supplementary considerations

Here we present supplementary considerations needed to close some of the loose ends in the simple treatment of the preceding section. The first is concerned with a possible critical anomaly of the shear viscosity, whose correlation function expression is

$$\eta = \frac{1}{k_B T} \int d\mathbf{r} \int_0^\infty dt \langle J^{xy}(\mathbf{r}, t) J^{xy}(0, 0) \rangle \tag{4.1}$$

where J^{xy} is the stress tensor in fluid. Here we follow the simple treatment of Perl and Ferrell (1972) and add to the free energy the following gradient term:

$$\frac{1}{2} K (\nabla\psi)^2 \tag{4.2}$$

where K is taken to be finite in this simple treatment. The anomalous contribution $\Delta\eta$ of the shear viscosity arises from the following mode-coupling part of J^{xy} :

$$J^{xy} \sim \frac{\partial\psi}{\partial x} \frac{\partial\Phi}{\partial(\partial\psi/\partial y)} = K \frac{\partial\psi}{\partial x} \frac{\partial\psi}{\partial y}. \quad (4.3)$$

Since ψ is denoted also as m_1 , we find

$$\Delta\eta = \frac{K^2}{k_B T} \frac{1}{(2\pi)^3} \int d\mathbf{k} \int_0^\infty dt k_x^2 k_y^2 |\langle m_1(\mathbf{k}, t) m_1(-\mathbf{k}, 0) \rangle / V|^2. \quad (4.4)$$

Now, according to the discussion at the end of § 3, the integrand of (4.4) persists at most for the times of the order of ξ^3 and thus we find

$$\Delta\eta \sim \xi^0 \quad (4.5)$$

which is finite or at most weakly divergent, the result which is known for pure and two-component fluids (Kadanoff and Swift 1968, Swift 1968).

Next we turn our attention to the assumption that only the viscous relaxation enters the intermediate states of \bar{L}_{ij} . The full expression for \bar{L}_{ij} in the matrix notation that includes the relaxation effects of diffusive modes in the intermediate states is

$$\bar{L} = \frac{2}{3(2\pi)^3} \int d\mathbf{k} \frac{1}{k^2} \chi(\mathbf{k})^{1/2} \cdot [v^* + \Gamma(k)]^{-1} \cdot \chi(\mathbf{k})^{1/2}. \quad (4.6)$$

First, it is clear that critical exponents of \bar{L} remain unaltered by the presence of $\Gamma(k)$ since it contains no divergence, but $\Gamma(k)$ cannot be ignored entirely because it contains finite matrix elements. Next, we consider the elements of \bar{L} which have previously been shown to diverge. Expanding (4.6) formally in powers of $\Gamma(k)$ we see that each term contains at least one small factor of Γ in view of (3.28), and hence $\Gamma(k)$ in (4.6) can be ignored for the diverging matrix elements of \bar{L} .

5. Discussion

In the preceding sections we have shown that tricritical divergences in the Onsager kinetic coefficients L_{ij} are ascribed to the divergence of a single coefficient \bar{L}'_{11} behaving as ξ and possibly also the weak divergence of \bar{L}'_{22} in the representation which diagonalizes the susceptibility matrix despite the fact that here we have an additional critical variable (the non-ordering variable (Riedel 1972)). This is simply due to the fact that critical fluctuations associated with the non-ordering variables are not strong enough to cause a clear divergence of \bar{L}'_{22} . These fluctuations, however, are strong enough to make \bar{L}'_{12} diverge in a representation in which $\chi_{12}(\mathbf{k}) \neq 0$. In general, when the fluctuations of the order parameter and those of the non-ordering variables are not statistically independent, we need two independent divergent kinetic coefficients $\bar{L}'_{11} \sim \xi$ and $\bar{L}'_{12} \sim \xi^{1/2}$ apart from possible weak divergences. If, however, there is a relation

$$\chi_{12}(\mathbf{k}) \simeq \frac{\chi_{12}(0)}{\chi_{11}(0)} \chi_{11}(\mathbf{k}), \quad (5.1)$$

we have

$$\bar{L}'_{12} \simeq \frac{\chi_{12}(0)}{\chi_{11}(0)} \bar{L}'_{11} \quad (5.2)$$

and transport anomalies near the tricritical point can be understood in terms of a single diffusion coefficient

$$D = \frac{k_B T}{\rho} \frac{\bar{\chi}_{11}}{\chi_{11}} \quad (5.3)$$

as in normal critical points of multicomponent fluids (Mistura 1972). This is also true if the coefficients of the transformation from $\{m_i\}$ to $\{m'_i\}$ are non-singular. At this moment we neither know whether this is true nor do we know about the validity of (5.1). It is of course simplest if possible to work throughout with the variables having a diagonal susceptibility matrix. In any event we have two 'degenerate' diffusion modes whose decay rates behave as ξ^{-3} near the tricritical point. We hope to come back to these questions and also to applications of this work to critical light scattering on another occasion.

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