Generalised hydrodynamics and Langevin equations for viscoelastic binary liquid mixtures

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Abstract. For viscoelastic binary liquid mixtures, generalised hydrodynamic equations are set up, in which the relaxation of the chemical potential due to structural relaxation is taken into account. A generalised diffusion equation is obtained, and the spectra of thermal fluctuations of concentration and mass density are derived. For very asymmetric mixtures of a mobile species in a very viscous solvent, such as a glass-forming liquid near its glass transition, coupled Langevin equations for concentration and mass density are derived, which may be applied to the calculation of the intensity of non-equilibrium fluctuations as observed in quench experiments.

1. Introduction

In very viscous binary liquid mixtures, slow structural relaxation can strongly influence the interdiffusion of the two molecular species over macroscopic length scales. The effect exists in very asymmetric mixtures, in which a mobile species is dissolved in a very viscous solvent. A typical case is the solution of small molecules in polymeric melts. In such systems, non-Fickian diffusion and sorption have been studied by a number of authors (Kishimoto *et al* 1960, Frisch 1962, Crank 1975, Durning 1985). The interdiffusion in very viscous polymer blends is a second, and more complicated, case (Meier and Strobl 1987, Strobl and Urban 1988, Schwahn *et al* 1990). A third example is the interdiffusion of the two metallic components in melts of ternary silicate glasses (Burnett and Douglas 1970, Frischat 1975, Mazurin and Porai-Koshits 1984).

In this paper we are mainly interested in the dynamics of thermal concentration fluctuations of long wavelength in such a system, which can be probed by light or neutron scattering or by small-angle x-ray scattering (Schroeder 1977, Jantzen *et al* 1981, Zarzycki and Naudin 1969, Craievich *et al* 1986). The concentration fluctuations described may occur either in a stable phase in thermal equilibrium or in the initial stage of spinodal decomposition in a two-phase region of the phase diagram.

The physical cause of the coupling between the structural relaxation and the diffusion process can be visualised as a swelling of the solvent medium upon penetration of the solute particles. It leads to coupled diffusion–relaxation modes, the frequency spectrum of which is shown in figure 1 for the case of a single-exponential relaxation with relaxation rate γ. The high-frequency diffusion coefficient $D(\infty)$ governs the diffusion in the unrelaxed structure, whereas the low-frequency coefficient $D(0)$, which is smaller than
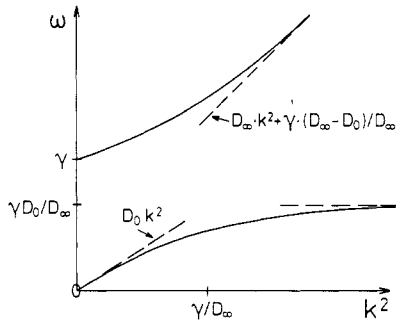
Figure 1. Frequency spectrum of coupled diffusion and relaxation modes (from Jäckle and Frisch 1985). $D(0)$ and $D(\infty)$ are the diffusion coefficients for low and high frequency (see text).

$D(\infty)$ as a result of Le Chatelier's principle (Landau and Lifshitz 1959, section 78), incorporates the effect of a structural adjustment of the solvent medium to a change of concentration.

To cover the effects of slow structural relaxation on diffusion, the hydrodynamic theory of diffusion in binary liquid mixtures (Cohen *et al* 1971, Lekkerkerker and Laidlaw 1973) needs to be generalised. An early contribution to generalised hydrodynamics of liquid mixtures, in which the projection operator formalism of microscopic theory was used, is due to Desai (1972). A generalised diffusion equation, which takes the relaxation of the chemical potential into account (Jäckle and Frisch 1985, 1986, see also Durning 1985), was derived within the framework of the phenomenological theory of thermo-viscoelasticity (Jäckle 1986, 1990). This equation has been applied to the early stage of spinodal decomposition (Binder *et al* 1986), where it leads to a generalisation of the theory of Cahn and Hilliard (see also Gupta 1985). As shown by Cook (1970), a complete description of the linear regime of spinodal decomposition must be based on hydrodynamic equations with fluctuations (Landau and Lifshitz 1959, ch XVII), i.e. Langevin equations. In a first paper (Jäckle and Pieroth 1988) this was achieved by introducing a relaxing internal variable, which is assumed to cause the relaxation of the chemical potential (Frisch 1964). However, the ambiguity of the definition of the internal variable leads to the occurrence of an ill defined parameter in the final formula for the time-dependent structure factor for the concentration fluctuations. Therefore, in the present paper, we aim to derive Langevin equations for well defined physical variables only.

The purpose of the paper is twofold. First we set up the generalised hydrodynamic equations for concentration c and mass density ρ (section 2), and derive the spectra of thermal fluctuations of these quantities (section 3), which can be measured by inelastic scattering of light and neutrons. Isothermal conditions are assumed. Considering thermal fluctuations, the effect of temperature fluctuations is assumed to be small compared with that of the concentration fluctuations. In section 4 the generalised diffusion equation is derived in which the coupling of structural relaxation to diffusion is taken into account. Secondly, the results obtained for the fluctuation spectra enable us to construct (in section 5) Langevin equations for the slow fluctuations of concentration and mass density, which are governed by diffusion and structural relaxation. These are the equations required for describing the temporal evolution of the *non-equilibrium fluctuations* of concentration and mass density observed in quench experiments. It is pointed out in the concluding section (section 6) that the new Langevin equations lead to the replacement of the ill defined coupling parameter occurring in the internal-variable

theory by a combination of measurable quantities. In the derivation of the Langevin equations the simplifying assumption is made that the relation between changes of the chemical potential and changes of concentration and mass density is instantaneous, and that only the viscoelastic stress–strain relation is a retarded constitutive equation. The validity of this assumption can be tested experimentally using the results of section 3. We expect the assumption to apply for very asymmetric solutions of a mobile species of particles in a very viscous solvent medium, in which the slow relaxation processes occur. In such a system the reaction of the solvent medium to concentration changes is retarded, whereas the mobile solute molecules should come to local equilibrium instantaneously.

2. Generalised hydrodynamic equations for viscoelastic binary liquid mixtures

It is convenient (Landau and Lifshitz 1959) to describe diffusion in a two-component liquid in terms of the concentration of one component, which is defined as

$$c = \rho_1/\rho \tag{2.1}$$

where ρ_1 and ρ are the mass densities of species 1 and of the mixture, respectively; ρ serves as the second variable. In the special situation considered in section 5, c is the concentration of the mobile particles, which contrast with the second species of molecules of the viscous host medium. According to irreversible thermodynamics (de Groot 1960), the thermodynamic driving force of the flux of concentration is proportional to $-\mathrm{grad}(\mu/T)$. The temperature T is treated as a constant. The chemical potential μ is defined by

$$\mu = \mu_1/m_1 - \mu_2/m_2 \tag{2.2}$$

in terms of the chemical potentials and masses (per particle) of the two components. The same is true for diffusion in an isotropic elastic medium, and, by interpolation, also in a viscoelastic medium. For isothermal conditions, this leads to the linearised diffusion equation in the form

$$\dot{c}(r, t) - M\Delta[\mu(r, t) + \mu_{\mathrm{ext}}(r, t)] = 0 \tag{2.3}$$

with a mobility M that is assumed to be constant. In equation (2.3) the effect of external potentials (per molecule) $V_{1,2}(r, t)$ is included in an 'external chemical potential' $\mu_{\mathrm{ext}}(r, t)$, which in analogy to (2.2) is defined as

$$\mu_{\mathrm{ext}} = V_1/m_1 - V_2/m_2. \tag{2.4}$$

The second equation for $c(r, t)$ and $\rho(r, t)$ is the linearised form of Newton's law, which reads

$$\rho_0 \dot{v}_\alpha = \nabla_\beta \sigma_{\alpha\beta} - n_0 \nabla_\alpha V_{\mathrm{ext}}. \tag{2.5}$$

Here v_α is the αth Cartesian component of the mean local velocity of the liquid mixture, and σ denotes the stress tensor, which can be decomposed into pressure P and shear stress $\sigma^{(s)}$ according to

$$\sigma_{\alpha\beta} = -\delta_{\alpha\beta} P + \sigma^{(s)}_{\alpha\beta}. \tag{2.6}$$

The external force term in (2.5) represents the sum of the external forces acting on both types of molecules and is given by

$$-n_0 \nabla V_{\mathrm{ext}} = -n_{1,0} \nabla V_1 - n_{2,0} \nabla V_2. \tag{2.7}$$

Here $n_{1,2}$ are the number densities of either species ($n = n_1 + n_2$). The index zero

denotes the mean equilibrium value for any quantity. In addition to equations (2.3) and (2.5), the linearised continuity equation

$$\dot{\rho}(r, t) + \rho_0 \, \text{div} \, v(r, t) = 0 \tag{2.8}$$

is needed to eliminate the longitudinal component of the velocity field $v(r, t)$.

The general equations of motion (2.3), (2.5) and (2.8) for concentration, mass density and velocity need to be supplemented by linear constitutive equations for chemical potential, pressure and shear stress. The deviation of the local chemical potential from the global equilibrium value, for example, can be expressed as

$$\delta\mu(r, t) = \mu_{|c}(0)\delta c(r, t) + [\mu_{|c}(\infty) - \mu_{|c}(0)] \int_{-\infty}^{t} \varphi_{\mu,c}(t - t')\dot{c}(r, t') \, \mathrm{d}t'$$

$$+ \mu_{|\rho}(0)\delta\rho(r, t) + [\mu_{|\rho}(\infty) - \mu_{|\rho}(0)] \int_{-\infty}^{t} \varphi_{\mu,\rho}(t - t')\dot{\rho}(r, t') \, \mathrm{d}t' \tag{2.9}$$

where $\mu_{|c}(0) = (\partial\mu/\partial c)_\rho^{(0)}$ and $\mu_{|c}(\infty) = (\partial\mu/\partial c)_\rho^{(\infty)}$ denote the low-frequency, i.e. thermodynamic, and high-frequency derivatives of the chemical potential with respect to the concentration, etc. The relaxation functions $\varphi_{\mu,c}(\tau)$ and $\varphi_{\mu,\rho}(\tau)$ describe the relaxation of the chemical potential after a step-like change of concentration and density at $\tau = 0$ from the initial to the final change. They are normalised by the condition $\varphi(\tau = 0) = 1$. Expression (2.9) is obtained using Boltzmann's superposition principle for after-effects in linear media.

Writing similar retarded constitutive equations for pressure and shear stress (Jäckle 1986), one obtains from equations (2.3), (2.5) and (2.8) the following generalised hydrodynamic equations for concentration and mass density:

$$\dot{c}(r, t) - M\Delta \left(\mu_{|c}(0)\delta c(r, t) + [\mu_{|c}(\infty) - \mu_{|c}(0)] \int_{-\infty}^{t} \varphi_{\mu,c}(t - t')\dot{c}(r, t') \, \mathrm{d}t' \right.$$

$$\left. + \mu_{|\rho}(0)\delta\rho(r, t) + [\mu_{|\rho}(\infty) - \mu_{|\rho}(0)] \int_{-\infty}^{t} \varphi_{\mu,\rho}(t - t')\dot{\rho}(r, t') \, \mathrm{d}t' \right)$$

$$= M\Delta\mu_{\text{ext}}(r, t) \tag{2.10a}$$

and

$$\ddot{\rho}(r, t) - \Delta \left(P_{|c}(0)\delta c(r, t) + [P_{|c}(\infty) - P_{|c}(0)] \int_{-\infty}^{t} \varphi_{P,c}(t - t')\dot{c}(r, t') \, \mathrm{d}t' \right.$$

$$\left. + c_c^2(0)\delta\rho(r, t) + [c_{l,c}^2(\infty) - c_c^2(0)] \int_{-\infty}^{t} \varphi_{\sigma_l,\rho}(t - t')\dot{\rho}(r, t') \, \mathrm{d}t' \right)$$

$$= n_0\Delta V_{\text{ext}}(r, t). \tag{2.10b}$$

Here

$$c_c^2(0) = P_{|\rho}(0) \tag{2.11}$$

defines the low-frequency sound velocity at constant concentration, which is the true

velocity of sound waves of low frequency, since diffusive modes do not couple to long-wavelength sound waves. The relaxation function $\varphi_{\sigma_l,\rho}(\tau)$ for longitudinal stress and the high-frequency longitudinal sound velocity $c_{1,c}(\infty)$ are defined by

$$[c_{1,c}^2(\infty) - c_c^2(0)]\varphi_{\sigma_1,\rho}(\tau) = [P_{|\rho}(\infty) - P_{|\rho}(0)]\varphi_{P,\rho}(\tau) + \tfrac{4}{3}[G(\infty)/\rho_0]\varphi_G(\tau) \qquad (2.12)$$

where $\varphi_{P,\rho}(\tau)$ and $\varphi_G(\tau)$ are relaxation functions occurring in the memory terms of the constitutive equations for pressure and shear stress, and $G(\infty)$ is the high-frequency shear modulus.

The generalised hydrodynamic equations (2.10) can be brought into a more compact form by taking the Fourier transform with respect to time and introducing frequency-dependent derivatives like

$$\mu_{|c}(\omega) = \mu_{|c}(0) - i\omega[\mu_{|c}(\infty) - \mu_{|c}(0)]\tilde{\varphi}_{\mu,c}(\omega) \qquad (2.13)$$

where $\tilde{\varphi}(\omega)$ denotes the Laplace transform of a relaxation function $\varphi(\tau)$:

$$\tilde{\varphi}(\omega) = \int_0^\infty d\tau\, e^{i\omega\tau}\varphi(\tau). \qquad (2.14)$$

Similarly, a frequency-dependent longitudinal modulus at constant concentration $C_{1,c}(\omega)$ is defined by

$$C_{1,c}(\omega)/\rho_0 = c_c^2(0) - i\omega[c_{1,c}^2(\infty) - c_c^2(0)]\tilde{\varphi}_{\sigma_1,\rho}(\omega). \qquad (2.15)$$

Using these definitions, the Fourier transform of equations (2.10a) and (2.10b) can be written as

$$[-i\omega - M\mu_{|c}(\omega)\Delta]c(\mathbf{r}, \omega) - M\mu_{|\rho}(\omega)\Delta\rho(\mathbf{r}, \omega) = M\Delta\mu_{\text{ext}}(\mathbf{r}, \omega) \qquad (2.16a)$$

and

$$-P_{|c}(\omega)\Delta c(\mathbf{r}, \omega) - \{\omega^2 + [C_{1,c}(\omega)/\rho_0]\Delta\}\rho(\mathbf{r}, \omega) = n_0\Delta V_{\text{ext}}(\mathbf{r}, \omega). \qquad (2.16b)$$

Concerning the frequency-dependent generalisations of thermodynamic derivatives and moduli, the following comments are in order. The frequency-dependent derivatives like $\mu_{|c}(\omega)$ (equation (2.13)) interpolate between the low- and high-frequency limits, which correspond to the thermodynamic derivatives for the liquid and for the isotropic elastic medium obtained by freezing the configurational degrees of freedom. Formula (2.15) interpolates between the hydrodynamic limit, which contains shear and bulk viscosities η and ζ and is given by

$$C_{1,c}^{\text{hydr}}(\omega) = \rho_0 c_c^2(0) - i\omega(\tfrac{4}{3}\eta + \zeta) \qquad (2.17)$$

and the high-frequency longitudinal sound velocity. Generalising formula (2.17) for arbitrary frequencies, one can introduce frequency-dependent shear and bulk viscosities as an alternative to using frequency-dependent elastic moduli. As a general rule, the thermodynamic relations between second derivatives of thermodynamic potentials also hold for the frequency-dependent quantities. We give the following examples, which are used in later sections. Again for the sake of a compact presentation, we introduce some further notations. We denote the frequency-dependent bulk modulus for constant concentration or chemical potential by $K_c(\omega)$ or $K_\mu(\omega)$, and the frequency-dependent

derivatives of the chemical potential with respect to the concentration at constant mass density or pressure by $B_v(\omega)$ or $B_P(\omega)$:

$$K_c(\omega) = \rho_0(\partial P/\partial \rho)_c^{(\omega)} \equiv \rho_0 P_{|\rho}(\omega) \tag{2.18a}$$

$$K_\mu(\omega) = \rho_0(\partial P/\partial \rho)_\mu^{(\omega)} \tag{2.18b}$$

$$B_v(\omega) = (\partial \mu/\partial c)_\rho^{(\omega)} \equiv \mu_{|c}(\omega) \tag{2.18c}$$

$$B_P(\omega) = (\partial \mu/\partial c)_P^{(\omega)}. \tag{2.18d}$$

Starting from retarded constitutive equations analogous to (2.9) for concentration and pressure in terms of changes of mass density and chemical potential, one derives the relation

$$K_c(\omega)/K_\mu(\omega) = B_v(\omega)/B_P(\omega) \tag{2.19}$$

which is analogous to the better known relation between the adiabatic and isothermal bulk moduli K_S and K_T and the specific heats c_v and c_P. Another example of interest is the generalised Maxwell relation

$$\mu_{|\rho}(\omega) = (1/\rho_0^2)P_{|c}(\omega) \tag{2.20}$$

which can be proved either in the framework of thermodynamic relaxation theory or using the Mori–Zwanzig projection operator formalism (Jäckle 1986). From (2.20) one derives the formula

$$K_c(\omega) - K_\mu(\omega) = [P_{|c}(\omega)]^2/[\rho_0 B_v(\omega)] \tag{2.21}$$

which, by (2.19), is equivalent to

$$B_v(\omega) - B_P(\omega) = [P_{|c}(\omega)]^2/[\rho_0 K_c(\omega)]. \tag{2.22}$$

The last equation is analogous to the relation between the difference of the specific heats c_P and c_v and the thermal expansion coefficient.

3. Dynamic susceptibilities and fluctuation spectra for concentration and mass density

Using linear response theory (Kadanoff and Martin 1963, Jäckle 1978), dynamic susceptibilities and fluctuation spectra are derived from our generalised hydrodynamic equations (2.10) in the usual way. The fluctuation–dissipation theory relates the fluctuation spectra $S_{x,y}(k, \omega)$ to the dynamic susceptibilities $\chi_{x,y}(k, \omega)$ by

$$S_{x,y}(k, \omega) = (2k_B T/\omega)\,\mathrm{Im}\,\chi_{x,y}(k, \omega). \tag{3.1}$$

The three dynamic susceptibilities $\chi_{c,c}(k, \omega), \chi_{c,\rho}(k, \omega)$ and $\chi_{\rho,\rho}(k, \omega)$ are obtained from the solution of the generalised hydrodynamic equations for $\delta c(r, t)$ and $\delta \rho(r, t)$ in the presence of plane-wave-like external perturbations $\mu_{ext}(r, t)$, $V_{ext}(r, t) \propto \exp[i(k \cdot r - \omega t)]$. The relation between this solution and the dynamic susceptibilities follows from the definitions of c, μ_{ext} and V_{ext} (equations (2.1), (2.4) and (2.7)) and reads

$$-\delta c(r, t) = \chi_{c,c}(k, \omega)\rho_0\mu_{ext}(r, t) + \chi_{c,\rho}(k, \omega)(n_0/\rho_0)V_{ext}(r, t) \tag{3.2a}$$

$$-\delta \rho(r, t) = \chi_{c,\rho}(k, \omega)\rho_0\mu_{ext}(r, t) + \chi_{\rho,\rho}(k, \omega)(n_0/\rho_0)V_{ext}(r, t). \tag{3.2b}$$

The results for the dynamic susceptibilities are given by

$$\chi_{c,c}(k, \omega) = (M/\rho_0)k^2/\{-i\omega + MB_v(\omega)k^2$$
$$- (M/\rho_0^2)[P_{|c}(\omega)]^2k^4/\{-\omega^2 + [C_{1,c}(\omega)/\rho_0]k^2\}\} \tag{3.3a}$$

$$\chi_{c,\rho}(k, \omega) = -(M/\rho_0)P_{|c}(\omega)k^4/[[-i\omega + MB_v(\omega)k^2]\{-\omega^2 + [C_{1,c}(\omega)/\rho_0]k^2\}$$

$$- (M/\rho_0^2)[P_{|c}(\omega)]^2k^4]] \qquad (3.3b)$$

$$\chi_{\rho,\rho}(k, \omega) = \rho_0 k^2/\{-\omega^2 + [C_{1,c}(\omega)/\rho_0]k^2$$

$$- (M/\rho_0^2)[P_{|c}(\omega)]^2k^4/[-i\omega + MB_v(\omega)k^2]\}. \qquad (3.3c)$$

The static limits $\chi_{x,y}(k, \omega = 0)$ of the susceptibilities, which determine the total intensity and correlation of mass density and concentration fluctuations ρ_k and c_k according to the fluctuation formula

$$\chi_{x,y}(k, \omega = 0) = \beta\langle x_k y_{-k}\rangle \qquad \beta = (k_BT)^{-1} \qquad (3.4)$$

are obtained in terms of thermodynamic derivatives as

$$\chi_{c,c}(k, \omega = 0) = 1/[\rho_0 B_P(0)] \qquad (3.5a)$$

$$\chi_{c,\rho}(k, \omega = 0) = (1/\rho_0)(\partial\rho/\partial\mu)_P^{(0)} \qquad (3.5b)$$

$$\chi_{\rho,\rho}(k, \omega = 0) = \rho_0^2/K_\mu(0). \qquad (3.5c)$$

The fluctuation spectra, which follow from expressions (3.3) using the fluctuation–dissipation theorem (3.1), display the contributions of longitudinal sound waves, diffusion and viscoelastic relaxation. Explicit expressions for the three separate contributions are derived in the limiting cases of rapid and slow relaxation, in which the average relaxation rate $\bar{\gamma}$ is much higher or much lower than the frequency of the longitudinal sound wave and of the diffusion mode for wavevector k:

$$\bar{\gamma} \gg c_{1,c}(0)k \qquad \text{for fast relaxation} \qquad (3.6a)$$

$$\bar{\gamma} \ll D(\infty)k^2 \qquad \text{for slow relaxation.} \qquad (3.6b)$$

In the first case (3.6a), referred to as the hydrodynamic limit, only sound waves and diffusion contribute to the fluctuation spectra. The hydrodynamic correlation functions for a binary liquid mixture including the contributions of heat conduction were calculated by Cohen *et al* (1971) and by Lekkerkerker and Laidlaw (1973). In our calculation, heat conduction is not taken into account. We assume here that heat conduction leads only to a relatively small contribution to the fluctuation spectra of concentration and mass density compared with the effect of particle diffusion, as we know that its contribution to the density fluctuation spectrum of viscoelastic one-component liquids is usually small. To obtain the hydrodynamic results, one has to replace all frequency-dependent quantities occurring in (3.3), except the longitudinal modulus $C_{1,c}(\omega)$, by their thermodynamic zero-frequency limits; the hydrodynamic expression for the longitudinal modulus contains the low-frequency sound velocity $c_c(0)$ at constant concentration and the shear and bulk viscosities η and ζ, and is given in equation (2.17). The following formulae are derived:

$$S_{c,c}^{\text{hydr}}(k, \omega) = \frac{2k_BT}{\rho_0 B_P(0)} \frac{D(0)k^2}{\omega^2 + [D(0)k^2]^2} \qquad (3.7a)$$

$$S_{c,\rho}^{\text{hydr}}(k, \omega) = \frac{2k_BT}{\rho_0(\partial\mu/\partial\rho)_P^{(0)}} \left(\frac{D(0)k^2}{\omega^2 + [D(0)k^2]^2} \right.$$

$$\left. - \frac{D(0)k^2\{\omega^2 - [c_c(0)k]^2\}}{\{\omega^2 - [c_c(0)k]^2\}^2 + [\omega k^2\Gamma(0)]^2} \right) \qquad (3.7b)$$

$$S_{\rho,\rho}^{\text{hydr}}(k,\omega) = \frac{2k_B T \rho_0^2}{K_\mu(0)}\left[\left(1 - \frac{B_P(0)}{B_v(0)}\right)\frac{D(0)k^2}{\omega^2 + [D(0)k^2]^2}\right.$$

$$+ \frac{B_P(0)}{B_v(0)}\frac{[c_c(0)k^2]^2\Gamma(0)}{\{\omega^2 - [c_c(0)k]^2\}^2 + [\omega k^2\Gamma(0)]^2}$$

$$\left.- \left(1 - \frac{B_P(0)}{B_v(0)}\right)\frac{D(0)k^2\{\omega^2 - [c_c(0)k]^2\}}{\{\omega^2 - [c_c(0)k]^2\}^2 + [\omega k^2\Gamma(0)]^2}\right]. \tag{3.7c}$$

The coefficient $\Gamma(0)$ given by

$$\Gamma(0) = (\tfrac{4}{3}\eta + \zeta)/\rho_0 + [B_v(0)/B_P(0) - 1]D(0) \tag{3.8}$$

determines the damping of the longitudinal sound waves. $D(0)$ is the zero-frequency limit of the frequency-dependent diffusion coefficient $D(\omega)$ defined in the following section (equations (4.7) and (4.13)). The expressions (3.7) are completely analogous to those for a one-component liquid (Kadanoff and Martin 1963), in which the contributions of heat conduction are replaced by those of particle diffusion in the binary mixture. Accordingly, in the density fluctuation spectrum (3.7c) the ratio of the intensity of the Rayleigh line due to diffusion to the intensity of the two Brillouin lines arising from sound waves is given by the analogue of the Landau–Placzek ratio, with the derivatives B_v and B_P of the chemical potential with respect to the concentration replacing the specific heats c_P and c_v (cf equation (2.22)):

$$I_R/I_B = B_v(0)/B_P(0) - 1. \tag{3.9}$$

In the opposite case (3.6b) of very slow relaxation, which we term the 'glassy limit', the slow viscoelastic relaxation contributes a narrow quasi-elastic line to the fluctuation spectra. In the spectrum of density fluctuations, this contribution is often called the 'Mountain line'. To obtain the contributions of sound waves and diffusion, all frequency-dependent quantities may be replaced by their high-frequency ($\omega \to \infty$) limits. The complete expressions for the fluctuation spectra in the glassy limit read

$$S_{c,c}^{\text{glassy}}(k,\omega) = \frac{2k_B T}{\rho_0}\left[\frac{1}{B_\sigma(\infty)}\frac{D(\infty)k^2}{\omega^2 + [D(\infty)k^2]^2} + \text{Im}\left(\frac{1}{\omega B_\sigma(\omega)}\right)\right] \tag{3.10a}$$

$$S_{c,\rho}^{\text{glassy}}(k,\omega) = 2k_B T\left[\frac{K_\mu(\infty)}{\rho_0 C_{1,\mu}(\infty)}\frac{1}{(\partial\mu/\partial\rho)_P^{(\infty)}}\left(\frac{D(\infty)k^2}{\omega^2 + [D(\infty)k^2]^2}\right.\right.$$

$$\left.- \frac{D(\infty)k^2\{\omega^2 - [c_{1,c}(\infty)k]^2\}}{\{\omega^2 - [c_{1,c}(\infty)k]^2\}^2 + [\omega k^2\Gamma(\infty)]^2}\right)$$

$$\left.- \frac{1}{\omega}\text{Im}\left(\frac{P_{1c}(\omega)}{B_\sigma(\omega)C_{1,c}(\omega)}\right)\right] \tag{3.10b}$$

$$S_{\rho,\rho}^{\text{glassy}}(k,\omega) = 2k_B T\rho_0^2\left\{\frac{1}{C_{1,\mu}(\infty)}\left[\left(1 - \frac{B_\sigma(\infty)}{B_v(\infty)}\right)\frac{D(\infty)k^2}{\omega^2 + [D(\infty)k^2]^2}\right.\right.$$

$$+ \frac{B_\sigma(\infty)}{B_v(\infty)}\frac{[c_{1,c}(\infty)k^2]^2\Gamma(\infty)}{\{\omega^2 - [c_{1,c}(\infty)k]^2\}^2 + [\omega k^2\Gamma(\infty)]^2}$$

$$\left.\left.- \left(1 - \frac{B_\sigma(\infty)}{B_v(\infty)}\right)\frac{D(\infty)k^2\{\omega^2 - [c_{1,c}(\infty)k]^2\}}{\{\omega^2 - [c_{1,c}(\infty)k]^2\}^2 + [\omega k^2\Gamma(\infty)]^2}\right]\right.$$

$$+ \frac{1}{\omega} \mathrm{Im} \left(\frac{1}{C_{1,\mu}(\omega)} \right) \bigg\}. \tag{3.10c}$$

The coefficient $\Gamma(\infty)$ of sound damping, which occurs in equations (3.10b, c), is given by

$$\Gamma(\infty) = [B_v(\infty)/B_\sigma(\infty) - 1]D(\infty). \tag{3.11}$$

In the glassy limit, there is only a contribution of diffusion to sound damping; the viscosity term is absent since 'phonon viscosity' is not taken into account. For the definition of the derivative $B_\sigma = D/M$ of the chemical potential with respect to the concentration, see equation (4.7). In each formula (3.10a–c) the last term describes the contribution of the slow viscoelastic relaxation. In the spectrum of concentration fluctuations (3.10a) the ratio of the intensity of the relaxation peak to that of the diffusion peak is

$$I_{\mathrm{rel}}/I_{\mathrm{diff}} = B_\sigma(\infty)/B_P(0) - 1. \tag{3.12}$$

In the spectrum of density fluctuation (3.10c) the relative intensities of the Brillouin lines, of the Rayleigh line due to diffusion and of the mountain line arising from relaxation are found to be

$$I_B/I_{\mathrm{tot}} = K_\mu(0)/C_{1,c}(\infty) \tag{3.13a}$$

$$I_R/I_{\mathrm{tot}} = [K_\mu(0)/C_{1,\mu}(\infty)][1 - B_\sigma(\infty)/B_v(\infty)] \tag{3.13b}$$

$$I_M/I_{\mathrm{tot}} = 1 - K_\mu(0)/C_{1,\mu}(\infty). \tag{3.13c}$$

In the glassy limit the Brillouin lines are shifted to higher frequencies compared with the hydrodynamic case, and their relative intensity is reduced. As for the Rayleigh line, its width is increased, and one also expects that its relative intensity is lower than the hydrodynamic result. In the analogous case of the Rayleigh line due to heat conduction in one-component liquids, the relative weight of the Rayleigh line, which is proportional to the square of the thermal expansion coefficient, is considerably reduced in the slow relaxation limit (Allain and Lallemand 1979, Sidebottom and Sorensen 1989, Jäckle 1990). It is not clear to us whether the Rayleigh line due to diffusion in binary mixtures generally shows the same behaviour. To indicate the factors involved, it is useful to quote the formula for a frequency-dependent 'Landau–Placzek ratio' for the Rayleigh line due to diffusion, which follows from equations (2.22) and (4.7):

$$\frac{K_\mu(0)}{C_{1,\mu}(\omega)} \left(1 - \frac{B_\sigma(\omega)}{B_v(\omega)} \right) = \frac{K_\mu(0)}{C_{1,\mu}(\omega)} \frac{[P_{|c}(\omega)]^2}{\rho_0 C_{1,c}(\omega) B_v(\omega)}. \tag{3.14}$$

Taken for $\omega = 0$ and $\omega = \infty$, this expression gives the relative intensity of the Rayleigh line in the hydrodynamic and in the glassy limit. If only the longitudinal moduli $C_{1,c}$ and $C_{1,\mu}$ in (3.14) are frequency-dependent (which case is assumed in section 5), the Landau–Placzek ratio shows the expected behaviour.
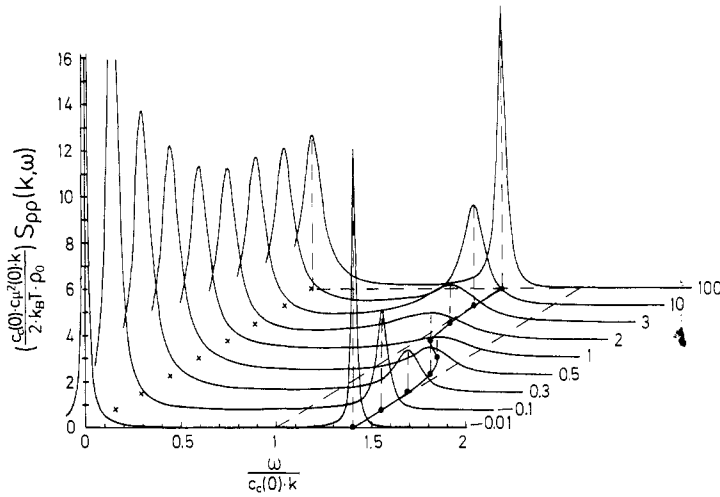
The relative intensities of the three contributions to the density fluctuation spectrum can easily be determined also for the intermediate case

$$D(0)k^2 \ll \bar{\gamma} \ll c_{1,c}(\infty)k. \tag{3.15}$$

In this limit the relative intensity of the Brillouin lines is also given by (3.13a), but (3.13b) and (3.13c) are replaced by

$$\frac{I_R}{I_{\mathrm{tot}}} = 1 - \frac{K_\mu(0)}{K_c(0)} = 1 - \frac{B_P(0)}{B_v(0)} \tag{3.16a}$$

$$\frac{I_M}{I_{\mathrm{tot}}} = K_\mu(0) \left(\frac{1}{K_c(0)} - \frac{1}{C_{1,c}(\infty)} \right). \tag{3.16b}$$

Figure 2. The density fluctuation spectrum of a viscoelastic binary mixture in dimensionless units. The number on each curve denotes the ratio $\gamma/[c_c(0)k]$ of relaxation rate and hydrodynamic sound frequency. For the values of the material parameters, see equation (3.17).

The result (3.16a) for the Rayleigh line agrees with the hydrodynamic Landau–Placzek formula (3.9). The intensity of the Mountain line given by (3.16b) compensates the loss of intensity of the Brillouin lines relative to the hydrodynamic case.

The intensity ratios (3.12), (3.13) and (3.16) are again analogous to results derived for a one-component liquid including heat conduction (Jäckle 1986, 1990).

In figure 2 we finally illustrate the gradual transition of the spectrum of density fluctuations $S_{\rho,\rho}(k, \omega)$ from the hydrodynamic to the glassy limit as a function of the temperature-dependent relaxation rate γ. The shift of the position of the Brillouin peak from the hydrodynamic sound frequency $c_c(0)k$ to the frequency $c_{1,c}(\infty)k$ in the glassy limit is marked. The strong broadening of the Brillouin line for $\gamma/[c_c(0)k] \simeq 1$ should also be noted. The curves are calculated for the purely viscoelastic case in which only the longitudinal modulus is frequency-dependent (cf section 5). A single relaxation rate γ is assumed. The plot depends on three dimensionless combinations of parameters, for which the following values are chosen:

$$M\mu_{|c}k^2/c_c(0)k = 0.1 \qquad c_{1,c}^2(\infty)/c_c^2(0) = 2 \qquad K_\mu(0)/K_c(0) = 0.6. \tag{3.17}$$

The last value corresponds to a Landau–Placzek ratio of $2/3$.

4. The generalised diffusion equation

We are mainly interested in situations in which particle diffusion and structural relaxation are the slowest processes occurring in the binary liquid. For given wavevector k such a situation occurs if the condition

$$Dk^2, \bar\gamma \ll D_T(\infty)k^2, c_{1,c}(\infty)k \tag{4.1}$$

is fulfilled, where $\bar\gamma$ is the average viscoelastic relaxation rate, and D and D_T denote

the coefficients of diffusion and thermal diffusivity. In this case, these processes are isothermal, and the condition of mechanical equilibrium

$$\nabla_\beta \sigma_{\alpha\beta} = n_0 \nabla_\alpha V_{\text{ext}} \tag{4.2}$$

holds. A spatial variation of the concentration leads to a local swelling (or contraction) of the liquid mixture compared with its equilibrium mass density ρ_0. The displacement field $u(r, t)$ caused by the swelling is determined by condition (4.2) and boundary conditions. We consider only the cases of an infinite medium and of a semi-infinite medium bounded by a plane. The deviation of the concentration from the equilibrium value is assumed to vanish at infinity. The external potential V_{ext} is dropped. Inserting the constitutive equations for P and $\sigma^{(s)}$ and taking the Fourier transform with respect to time, we can write the condition of mechanical equilibrium (4.2) as

$$C_{1,c}(\omega) \,\text{grad div}\, u(r, \omega) + i\omega G(\infty)\bar{\varphi}_G(\omega) \,\text{rot rot}\, u(r, \omega)$$

$$= P_{|c}(\omega) \,\text{grad}\, c(r, \omega). \tag{4.3}$$

This equation has the solution

$$\text{div}\, u(r, \omega) = \frac{P_{|c}(\omega)}{C_{1,c}(\omega)} c(r, \omega) \qquad \text{rot}\, u(r, \omega) = 0. \tag{4.4}$$

Using

$$\text{div}\, u(r, \omega) = -\rho(r, \omega)/\rho_0 \tag{4.5}$$

we obtain for the variation of the chemical potential

$$\mu(r, \omega) = B_\sigma(\omega) c(r, \omega) \tag{4.6}$$

with an effective frequency-dependent derivative of μ with respect to c given by

$$B_\sigma(\omega) = B_v(\omega) + [B_P(\omega) - B_v(\omega)]K_c(\omega)/C_{1,c}(\omega) \tag{4.7}$$

where $B_v(\omega)$ and $B_P(\omega)$ are given by (2.18c) and (2.22). It is useful to note the following relation for $B_\sigma(\omega)$, similar to equation (2.19):

$$B_v(\omega)/B_\sigma(\omega) = C_{1,c}(\omega)/C_{1,\mu}(\omega). \tag{4.8}$$

The frequency-dependent longitudinal modulus at constant chemical potential $C_{1,\mu}(\omega)$ occurring in this relation is obtained by replacing $K_c(\omega)$ by $K_\mu(\omega)$ in the expression for $C_{1,c}(\omega)$ (equation (2.15)):

$$C_{1,\mu}(\omega) = K_\mu(\omega) - i\omega \tfrac{4}{3} G(\infty)\bar{\varphi}_G(\omega). \tag{4.9}$$

Writing $B_\sigma(\omega)$ as

$$B_\sigma(\omega) = B_P(0) + [B_\sigma(\infty) - B_P(0)](-i\omega)\bar{\varphi}_{\mu,c;\sigma}(\omega) \tag{4.10}$$

we define a relaxation function $\varphi_{\mu,c;\sigma}(\tau)$ by its Laplace transform. Using this representation, the inverse Fourier transform of (4.6) yields

$$\delta\mu(r, t) = B_P(0)\delta c(r, t) + [B_\sigma(\infty) - B_P(0)] \int_{-\infty}^{t} \varphi_{\mu,c;\sigma}(t - t')\dot{c}(r, t')\,\mathrm{d}t'. \tag{4.11}$$

Combined with equation (2.3), this leads to the generalised diffusion equation

$$\dot{c}(r, t) - D(0)\Delta c(r, t) - [D(\infty) - D(0)] \int_{-\infty}^{t} \varphi_{\mu,c;\sigma}(t - t')\Delta\dot{c}(r, t')\,\mathrm{d}t'$$

$$= M\Delta\mu_{\text{ext}}(r, t) \tag{4.12}$$

with the frequency-dependent diffusion coefficient defined by

$$D(\omega) = MB_\sigma(\omega). \tag{4.13}$$

Calculating the dynamic susceptibility $\chi_{c,c}(k, \omega)$ from (4.12) indeed yields expression (3.3a) without the $-\omega^2$ term in the denominator.

5. Langevin equations for coupled processes of diffusion and swelling in a Maxwellian model

In the following we consider a simplified viscoelastic model in which only the relations between pressure and mass density, and between shear stress and strain, are retarded. The response of the chemical potential to changes of c and ρ is assumed to be instantaneous. Consequently, only bulk and longitudinal elastic moduli are frequency-dependent; the derivatives $\mu_{|c}$ and $\mu_{|\rho} = P_{|c}/\rho_0^2$ are constants. The validity of these assumptions needs to be tested experimentally by measuring the spectra of density and concentration fluctuations and comparing them with the general results given in section 3. As already mentioned, we expect this simplification to be appropriate for the solution of a mobile species of particles in a very viscous solvent. In such a system the only effect of structural relaxation should be the retarded swelling of the host medium, which follows all changes of concentration of the mobile particles; for given swelling, which is described by the mass density $\rho(r, t)$, the response of the mobile particles should obey the ordinary diffusion equation with a drift term allowing for the inhomogeneity of the medium. The viscoelastic retardation of the swelling causes the diffusion constant at high and low frequencies to be different. From (4.7), (2.18c), (2.22) and (4.13) we obtain for the difference

$$D(\infty) - D(0) = [M(P_{|c})^2/\rho_0](1/K_c(0) - 1/C_{1,c}(\infty)). \tag{5.1}$$

We mention that the simplified model introduced in this section is analogous to Zwanzig's explanation (Zwanzig 1988) of a frequency-dependent specific heat $c_P(\omega)$ of viscoelastic liquids, in which only the dispersion of the isothermal longitudinal modulus, $C_{1,T}$ (or equivalently of a frequency-dependent longitudinal viscosity) is taken into account. It has been pointed out (Jäckle 1990), however, that Zwanzig's model is not in agreement with experimental data for certain viscous liquids near the glass transition. As a further simplification, the relaxation of pressure and shear stress is assumed to be exponential and described by the same function

$$\varphi_{P,n}(\tau) = \varphi_G(\tau) = \exp(-\gamma\tau). \tag{5.2}$$

It is shown that for this model the concentration and the mass density obey two coupled differential equations, which are of first order in time. We subsequently construct the stochastic force terms to obtain Langevin equations for the slow processes in a viscoelastic mixture with fluctuations.

Under the conditions stated above, we obtain from (4.4) and (4.5)

$$-\rho(r, \omega)/\rho_0 = P_{|c}\left[\frac{1}{K_c(0)} + \left(\frac{1}{C_{1,c}(\infty)} - \frac{1}{K_c(0)}\right)\frac{-i\omega}{-i\omega + \gamma'}\right]c(r, \omega) \tag{5.3}$$

with a new relaxation rate γ' given by

$$\gamma'/\gamma = K_c(0)/C_{1,c}(\infty). \tag{5.4}$$

Taking the inverse Fourier transform of (5.3) with respect to time yields the following

relation between $\delta\rho(t)$ and $\delta c(t)$, which describes the retarded swelling of the material after changes in concentration:

$$-\delta\rho(r, t)/\rho_0 = P_{|c}\left[\frac{1}{K_c(0)}\,\delta c(r, t) + \left(\frac{1}{C_{1,c}(\infty)} - \frac{1}{K_c(0)}\right)\right.$$

$$\left. \times \int_{-\infty}^{t} e^{-\gamma'(t-t')}\dot{c}(r, t')\,dt'\right]. \tag{5.5}$$

From this equation the desired differential equation is found after differentiating with respect to time and eliminating the integral term. The differential equation has the form of a relaxation equation and reads

$$\frac{\partial}{\partial t}\left(\delta\rho(r, t) + \rho_0\frac{P_{|c}}{C_{1,c}(\infty)}\,\delta c(r, t)\right) = -\gamma'\left(\delta\rho(r, t) + \rho_0\frac{P_{|c}}{K_c(0)}\,\delta c(r, t)\right). \tag{5.6}$$

On the LHS of this equation we identify the retarded change of the mass density, which is due to swelling, as

$$\delta\rho_{\text{ret}} = \delta\rho + \rho_0(P_{|c}/C_{1,c}(\infty))\delta c. \tag{5.7}$$

The second differential equation is the ordinary diffusion equation with a term proportional to $\mu_{|\rho}\delta\rho(r, t)$ describing the feedback between $\delta\rho$ and δc:

$$\dot{c}(r, t) - M\Delta[\mu_{|c}\delta c(r, t) + \mu_{|\rho}\delta\rho(r, t)] = 0. \tag{5.8}$$

Taking the spatial Fourier transform and introducing the two-vector

$$x(t) = (c_k(t), \rho_{\text{ret},k}(t)) \tag{5.9}$$

the two equations (5.6) and (5.8) can be written as

$$\dot{x}(t) + \mathbf{\Omega}x(t) = 0 \tag{5.10}$$

with the dynamic matrix $\mathbf{\Omega}$ defined by

$$\mathbf{\Omega} = \begin{pmatrix} D(\infty)k^2 & M\mu_{|\rho}k^2 \\ \gamma'\rho_0 P_{|c}[1/K_c(0) - 1/C_{1,c}(\infty)] & \gamma' \end{pmatrix} \tag{5.11}$$

where $D(\infty)$ is given by (4.7) and (4.13)

$$D(\infty)/M = \mu_{|c} - (P_{|c})^2/[\rho_0 C_{1,c}(\infty)]. \tag{5.12}$$

We now add stochastic force terms $(\eta_0(t), \eta_1(t))$ describing Gaussian white noise to the RHS of the set (5.10) of deterministic differential equations. The stochastic differential equations read

$$\dot{x}(t) + \mathbf{\Omega}x(t) = \boldsymbol{\eta}(t). \tag{5.13}$$

The intensity of the stochastic forces is determined by the kinetic (or Onsager) coefficients L_{ij} according to

$$\langle\eta_i(t)\eta_j^*(t')\rangle = 2k_B TL_{ij}\delta(t - t'). \tag{5.14}$$

We are left with the problem of calculating the matrix of kinetic coefficients L_{ij} associated with the set of first-order differential equations (5.10). If $S_{ij} = \langle x_i x_j^*\rangle$ denotes the

elements of the covariance matrix for the thermal fluctuations of the variables (5.9), the formula for **L** is (Fox 1978)

$$\mathbf{L} = \mathbf{\Omega S}/(k_B T).\tag{5.15}$$

All depends now on the right use of this formula. The point one must be aware of is that only the *slow* fluctuations described by the stochastic differential equations (5.13) must be included in the covariance matrix in formula (5.15), whereas thermodynamic fluctuation formulae give the *total* intensity of thermal fluctuations. Therefore the thermodynamic fluctuation formula

$$\langle |\rho_k|^2 \rangle = k_B T \chi_{\rho,\rho}(k, \omega = 0) = k_B T(\rho_0^2/K_\mu(0))\tag{5.16}$$

for the total intensity of the mass density fluctuations must *not* be used for S_{11}, since it includes the contribution of the longitudinal sound waves (and of the heat conduction mode), which are not described by (5.10). Subtracting the sound-wave contribution, we obtain for the intensity of the slow mass density fluctuations

$$\langle |\rho_k|^2 \rangle_{\text{slow}} = k_B T \rho_0^2 (1/K_\mu(0) - 1/C_{1,c}(\infty)).\tag{5.17}$$

Using this expression, after some algebra one finds the following result for **L**:

$$\mathbf{L} = \begin{pmatrix} Mk^2/\rho_0 & \sigma \\ \sigma & \gamma'\rho_0^2[1/K_c(0) - 1/C_{1,c}(\infty)] \end{pmatrix}.\tag{5.18}$$

The matrix of kinetic coefficients is diagonal. The coefficient L_{00} is the same as in the Cahn–Hilliard–Cook equation (Cook 1970). The interesting point is that the coefficient L_{11}, which determines the strength of the stochastic forces acting on the retarded change $\delta\rho_{\text{ret}}$ of the mass density, is given by measurable viscoelastic parameters. In terms of the low- and high-frequency longitudinal sound velocities $c_c(0)$ and $c_{1,c}(\infty)$, the formula for L_{11} can be written as

$$L_{11} = \gamma'\rho_0(1/c_c^2(0) - 1/c_{1,c}^2(\infty)).\tag{5.19}$$

If, on the other hand, formula (5.16) had been used in evaluating equation (5.15), the result would have been an asymmetric **L** matrix, which is obviously wrong. We note that, apart from the contribution of $G(\infty)$ to $C_{1,c}(\infty)$, the result (5.18) can also be obtained directly from the internal-variable theory (Jäckle and Pieroth 1988) by defining $\delta\rho_{\text{ret}}$ as

$$\delta\rho - (\partial\rho/\partial c)_\xi \delta c = (\partial\rho/\partial\xi)_c \delta\xi\tag{5.20}$$

and using the relations between thermodynamic derivatives involving ξ and parameters of the viscoelastic constitutive equations.

For completeness, we finally write down the coupled Langevin equations for the full density change $\delta\rho$ instead of the retarded part $\delta\rho_{\text{ret}}$ as second variable. Defining a two-vector

$$\tilde{x}(t) = (c_k(t), \rho_k(t))\tag{5.21}$$

they can again be written in the form of equation (5.12) but with a different dynamic matrix $\tilde{\mathbf{\Omega}}$ given by

$$\tilde{\mathbf{\Omega}} = \begin{pmatrix} M\mu_{|c}k^2 & M\mu_{|\rho}k^2 \\ P_{|c}\rho_0[\gamma'/K_c(0) - M\mu_{|c}k^2/C_{1,c}(\infty)] & \gamma' - Mk^2(P_{|c})^2/\rho_0 C_{1,c}(\infty) \end{pmatrix}\tag{5.22}$$

and a new matrix $\tilde{\mathbf{L}}$ of kinetic coefficients, which reads

$$\tilde{\mathbf{L}} = \begin{pmatrix} Mk^2/\rho_0 & -Mk^2(P_{|c}/C_{1,c}(\infty)) \\ -Mk^2(P_{|c}/C_{1,c}(\infty)) & \gamma'\rho_0^2[1/K_c(0) - 1/C_{1,c}(\infty)] + Mk^2\rho_0[P_{|c}/C_{1,c}(\infty)]^2 \end{pmatrix}.\tag{5.23}$$

6. Concluding remarks

The results derived in this paper are relevant for two different types of experiment. First, we have calculated the fluctuation spectra of long-wavelength fluctuations of the concentration and the mass density, which can be probed by inelastic light scattering (Demoulin *et al* 1974, Schroeder 1977, Sidebottom and Sorensen 1989). Secondly, we derived Langevin equations, from which the temporal evolution of the intensity of these same fluctuations in quench experiments can be derived. The fact that the variables used in our description are physically well defined and only measurable parameters enter removes a deficiency of our earlier internal-variable theory (Jäckle and Pieroth 1988). In the expression for the time-dependent structure factor for the concentration fluctuations, which is valid in the linear regime, a coupling parameter λ entered, which was related to the ill defined internal variable and could not be calculated in terms of measurable physical quantities. Our new Langevin equations (5.10), on the other hand, lead to the same result with λ replaced by the combination

$$(\partial\rho/\partial c)_P^{(0)}\left(1 - K_c(0)/C_{1,c}(\infty)\right)$$ (6.1)

of measurable thermodynamic and viscoelastic parameters (Pieroth 1989).

Acknowledgment

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