Stress tensor correlation functions and elastic moduli for an interface—a continuous model approach

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Received 12 March 1984, in final form 8 May 1984

Abstract. Using the continuous or field-theoretical model we have calculated stress tensor correlation functions and elastic moduli for a system containing an interface. The shortcomings of this approach as well as its possible applications are discussed.

The detailed understanding of the properties of an interface separating bulk phases of a material is important for explanation of a variety of phenomena happening in the course of phase transformations.

Recently there has been growing interest in the properties of interfaces which has been stimulated by an attempt to describe critical properties of a system via the analysis of its interface behaviour. These attempts turn out to be quite successful in both equilibrium and non-equilibrium case (Bausch et al 1982, Zia 1983).

The important role in these works is played by the so-called capillary waves model introduced originally by Buff et al (1965) to account for the properties of a liquid–vapour interface in the presence of an external gravitational field. A very interesting analysis of the role of an external field was given by Zittartz (1967). A recent critical appraisal of these models has been given by Evans (1981).

The dynamical theory of interfaces has been also developed during the last few years beginning with Felderhof's (1970) analysis of the van der Waals interface and the recent capillary waves theory of Turski and Langer (1980). Recently the Mori–Zwanzig memory functions approach to studying interface dynamics has been pursued by Grant (1982), Grant and Desai (1983) and Baus and Tejero (1983). A variant theoretical approach has been proposed by Zielinska and Bedeaux (1982).

Independently of these approaches several attempts were made to describe the interface within the scope of molecular theory. A review has been given by Jhon et al (1981).

In a recent paper along that line Baus (1982) pointed out that at high frequencies a liquid–vapour interface should exhibit more elastic properties than these described by the surface tension alone. Using a generalisation of the Schofield (1966) and Zwanzig and Mountain (1965) theory of elastic moduli for a homogeneous fluid, Baus has analysed the high-frequency response of a liquid–vapour interface and concluded that in addition to modified bulk modulus and simple surface tension the interface possesses three additional elastic moduli reflecting the anisotropy of the interface reaction.
In the long-wavelength limit one should be able to make a connection between the Baus theory and the field theoretical or continuous model analysis which is more customary in interfacial physics. Below we shall present such an analysis of the elastic moduli of an interface.

The model we shall use in this work is basically the isothermal version of the model used in the hydrodynamical theory of nucleation (Langer and Turski 1973).

Since we are interested in the high-frequency response of an interface, such an approach seems to be justified. For discussion of this point see Turski and Langer (1980), Grant (1982), Grant and Desai (1983) and Baus and Tejero (1983). The analysis for the quantum solid-superfluid liquid interface presented recently by Andreev (1982) indicates that our model contains the essential ingredients needed in that theory. For example the spectrum of the crystallisation waves is essentially the same as that of 'isothermal' capillary waves discussed in Turski and Langer (1980).

The basic quantity we need is the free energy functional which we shall use in the same form as in Langer and Turski (1973); see also Evans (1981). We write:

\[ F(n, u) = F_K(n, u) + F_V(n) = \frac{1}{2} \int m n u^2 \, d^3r + \int \omega(n, \nabla n) \, d^3r \]

(1)

where

\[ \omega(n, \nabla n) = \frac{1}{2} K (\nabla n)^2 + f(n) - \mu_0 n + n V_{ext}. \]

(2)

In equation (2) \( f(n) \) is the free energy per unit volume of homogeneous fluid, \( \mu_0 \) is the chemical potential, \( K \) is the so-called gradient energy coefficient and \( V_{ext} \) is the external potential. We can assume that \( V_{ext} \) is an external gravitational field but in practice it will be convenient to have in mind the Zittartz potential (Zittartz 1967).

The planar interface separating liquid from its vapour corresponds to unidirectionally inhomogeneous solution of the equation \( \delta F/\delta n = 0 \). This equation was thoroughly studied in the literature (see Yang et al 1976). For the van der Waals choice of the \( f(n) \), i.e. \( f(n) = -\kappa n^2 + \omega n^4 \) and for the Zittartz potential \( V_{Z, ext} \) one obtains the well-known tanh-like density profile.

In order to study the elastic properties of the interface we write the equation of motion for the fluid in the form

\[ \delta_t n u_\beta = -\nabla_\beta \sigma_{\alpha\beta} - n \nabla_\beta V_{ext} \]

(3)

where the stress tensor \( \sigma_{\alpha\beta} \) is given as

\[ \sigma_{\alpha\beta} = \sigma^{K}_{\alpha\beta} + \sigma^{V}_{\alpha\beta} = n u_\alpha u_\beta + \sigma^{V}_{\alpha\beta} \]

(4)

and

\[ \sigma^{V}_{\alpha\beta} = K n \nabla_\alpha n \nabla_\beta n - \delta_{\alpha\beta} \omega + n \delta_{\alpha\beta} \left( \frac{\partial}{\partial n} - \nabla_\alpha \frac{\partial}{\partial \nabla_\beta n} \right) \omega. \]

(5)

Note that in the paper of Yang et al the last term in the expression (5) was missing.

It is elementary to check that the solutions of equation \( \delta F/\delta n = 0 \) are equivalent to these of stationary form of equation (3). Following the standard linear response analysis we shall assume that the density field \( \hat{n}(z) \) and the velocity field \( u = 0 \) are perturbed and we shall denote the deviations of the density and velocity fields as \( n(x), u(x) \) respectively. The fluctuations of the kinetic and potential parts of the stress tensor are given as

\[ \delta \sigma^{K}_{\alpha\beta} = \hat{n}(z) u_\alpha(x) u_\beta(x) \]

(6)
Stress tensor correlation functions

\[ \delta \sigma^{(r)}_{\alpha\beta} = 2K \nabla_{(\alpha} \hat{h} \nabla_{(\beta}) \nu + \delta_{\alpha\beta} \hat{h}(z) \hat{H}(x) \nu(x) \]  

where

\[ \hat{H}(z) = \frac{\partial^2 f}{\partial n(z)} - K \nabla^2 \]

and as usual \( A_{(\alpha\beta)} = (A_{\alpha\beta} + A_{\beta\alpha})/2 \). Strictly speaking \( \delta \sigma^{(r)}_{\alpha\beta} \) contains yet another term

\[ -\delta_{\alpha\beta} K \frac{d}{dz} \left( \frac{d\hat{n}}{dz} \nu(x) \right) \]

which does not contribute to the correlation functions we are going to study, so it can be omitted.

Consider now a general inhomogeneous fluid subject to an instantaneous deformation described by a deformation tensor \( \varepsilon_{\alpha\beta}(r) \). The excess free energy \( \Delta F \) associated with that deformation is

\[ \Delta F = \frac{1}{2} \int d^d r \int d^d r' \varepsilon_{\alpha\beta}(r) C_{\alpha\beta\alpha'\beta'}(r, r') \varepsilon_{\alpha'\beta'}(r') \]

where the matrix \( C_{\alpha\beta\alpha'\beta'}(r, r') \) is the matrix of generalised elastic moduli for the fluid.

The stress tensor \( \delta \sigma_{\alpha\beta} \) is related to the deformation \( \varepsilon_{\alpha\beta} \) by

\[ \delta \sigma_{\alpha\beta}(r) = \int d^d r' C_{\alpha\beta\alpha'\beta'}(r, r') \varepsilon_{\alpha'\beta'}(r'). \]

Following standard arguments the probability of realisation of the field \( \sigma_{\alpha\beta} \) is proportional to \( \exp(-\Delta F/k_B T) \); thus the matrix \( C_{\alpha\beta\alpha'\beta'} \) can be expressed in terms of the stress tensor correlation function as follows:

\[ C_{\alpha\beta\alpha'\beta'}(r, r') = (\delta \sigma_{\alpha\beta}(r) \delta \sigma_{\alpha'\beta'}(r'))/k_B T. \]

Since the lowest-order non-vanishing contribution to the \( \delta \sigma^F \) is already quadratic in the velocity field fluctuations, equation (6), neither \( (\delta \sigma^F \delta \sigma^F) \) nor \( (\delta \sigma^F \delta \sigma^E) \) contribute to the correlation function (11) within the linear response approximation. For homogeneous fluid this function is translationally invariant and the 'true' elastic coefficients are obtained from its Fourier transform via:

\[ C_{\alpha\beta\alpha'\beta'}^F = \lim_{q \to 0} \tilde{C}_{\alpha\beta\alpha'\beta'}(q). \]

In the case of a planar interface the fluid still has translational invariance in the interface plane. Let \( \mathbf{R} \) denote a \((d - 1)\)-dimensional vector in that plane and let \( \mathbf{Q} \) be a similar vector in the Fourier space. We write then \( C_{\alpha\beta\alpha'\beta'}(r, r') = C_{\alpha\beta\alpha'\beta'}(\mathbf{R}, z, z') \) and the elastic coefficients for a system with an interface are defined as follows:

\[ \tilde{C}_{\alpha\beta\alpha'\beta'} = \lim_{Q \to 0} \int_{-\infty}^{+\infty} d z \int_{-\infty}^{+\infty} d z' \tilde{C}_{\alpha\beta\alpha'\beta'}(\mathbf{Q}, z, z'). \]

The interfacial elastic coefficients \( E_{\alpha\beta\alpha'\beta'} \) are now defined as the difference between these obtained from equation (14) and those calculated for the same system via the Gibbs construction, that is

\[ C_{\alpha\beta\alpha'\beta'}^I = C_{\alpha\beta\alpha'\beta'}^F (1 - \theta(z)) + C_{\alpha\beta\alpha'\beta'}^F \theta(z) \]

where the distance \( z \) is measured from the Gibbs dividing surface and \( C_{\alpha\beta\alpha'\beta'}^{(V)} \) are the elastic coefficients for homogeneous liquid and vapour phase respectively. Close to \( T_c \), \( C_{\alpha\beta\alpha'\beta'}^I \approx C_{\alpha\beta\alpha'\beta'}^F \) as calculated for a one-phase system.
The number of independent coefficients in the correlation matrix \( C_{\alpha\beta, \alpha'\beta'} \) depends on the space dimensionality and the number of symmetries the system has. For \( d = 3 \), the symmetry of the stress tensor reduces the number of independent components of \( C_{\alpha\beta, \alpha'\beta'} \) from 81 to 21. Further reduction is achieved by carefully counting the number of rotational symmetries broken by the interface. The final number of these independent coefficients is then five and Baus (1982) has given a molecular level expression for these coefficients in the absence of an external field. We derive explicit expressions for the matrix elements \( C_{\alpha\beta, \alpha'\beta'} \) using the stress tensor fluctuations (2.9). We obtain

\[
C_{\alpha\beta, \alpha'\beta'}(R, z_1, z_2) = \delta_{\alpha\beta} \delta_{\alpha'\beta'} \tilde{h}(z_1) \tilde{h}(z_2) \tilde{H}(R, z_1) \tilde{H}(R, z_2) \langle \nu(R_1, z_1), \nu(R_2, z_2) \rangle \\
+ 2K \delta_{\alpha\beta} \tilde{h}(z_1) (d\tilde{h}/dz_2) \tilde{H}(R, z_1) \tilde{H}(R, z_2) \langle \nu(R_1, z_1), \nabla(\nu(R_2, z_2), \nu(R_2, z_2)) \delta_{\alpha\beta} \rangle \\
+ \text{term with } z \rightarrow z' \text{ and } (\alpha\beta) \rightarrow (\alpha'\beta') \\
+ 4K^2 (d\tilde{h}/dz_1)(d\tilde{h}/dz_2) \delta_{\alpha\beta} \langle \nabla(\nu(R_1, z_1), \nabla(\nu(R_2, z_2), \nu(R_2, z_2) \delta_{\alpha\beta}) \rangle.
\]

(14)

The expression (14) tells us that the elastic moduli of our system are completely determined by the order parameter correlation function \( G(R, z_1, z_2) = \langle \nu(R_1, z_1), \nu(R_2, z_2) \rangle \). For a homogeneous system expression (14) simplifies and one gets:

\[
C_{\alpha\beta, \alpha'\beta'}^{0}(g) = \delta_{\alpha\beta} \delta_{\alpha'\beta'} \langle n_g K_T \rangle^{-2} (1 + \xi^2 Q^2) \langle \tilde{v}_q \tilde{v}_{-q} \rangle
\]

(15)

where \( K_T \) is the isothermal compressibility of the fluid, \( \xi \) is the mean-field correlation length and \( \langle \tilde{v}_q \tilde{v}_{-q} \rangle \) is the mean-field order parameter correlation function. It is easy to see now that one recovers a standard expression for bulk modulus by taking the \( g \rightarrow 0 \) limit of equation (15). Indeed,

\[
\lim_{g \rightarrow 0} C_{\alpha\beta, \alpha'\beta'}^{0}(g) = \delta_{\alpha\beta} \delta_{\alpha'\beta'} (1/K_T).
\]

Equation (15) also shows the main drawback of the theory based on functional (1). This model does not describe correctly the transverse motion of the fluid (no viscosity), thus it cannot account for the shear modulus of a homogeneous fluid. However, as indicated above, this model may account correctly for the averaged properties of a solid-helium-superfluid-liquid interface.

In order to calculate elastic moduli in the presence of an interface one needs the explicit form of \( G(R, z_1, z_2) \). The mean-field expressions for this function were discussed by Zittartz (1967) and Evans (1981). We shall use in what follows the weak-gravitational-field limit of \( G \) as discussed by Evans (1981) but all the results can also be obtained using the Zittartz potential \( V_g \), and his \( G \) although after more complicated algebra.

Thus our expression for \( G \) reads:

\[
G(Q, z_1, z_2) = k_B T (mg \Delta n)^{-1} (1 + l^2 Q^2)^{-1} \left( \frac{d\tilde{h}}{dz_1} \right) \left( \frac{d\tilde{h}}{dz_2} \right) \\
+ \frac{k_B T}{K} \sum_{s>0} \psi_s(z_1) \psi_s(z_2) \frac{\psi_s(z_1) \psi_s(z_2)}{E_s + Q^2},
\]

(16)

where \( \Delta n \) is the difference between the liquid and vapour densities, \( l \) is the capillary length equal to \( (\gamma_{\text{vDW}}/mg \Delta n)^{1/3} \), \( \gamma_{\text{vDW}} \) being the van der Waals surface tension, \( \gamma_{\text{vDW}} = K f (d\tilde{h}/dz)^2 dz \), \( E_s \) and \( \psi_s \) are the eigenvalues and eigenfunctions of the operator \( \hat{H}(Q, z) \) respectively. Since \( \psi_s \) are orthogonal to the ground-state wavefunction \( d\tilde{h}/dz \), inserting the expression (16) into equation (14) simplifies the algebra considerably, since
most of the terms will vanish after the integration over \( z_1 \) and \( z_2 \) (see equation (15)). The first term on the rhs of equation (16) gives the diagonal elastic coefficient which we shall call \( \kappa \). Explicitly

\[
\kappa = \lim_{Q \to 0} \int \int_{-\infty}^{\infty} d z_1 \ d z_2 \hat{n}(z_1) \hat{n}(z_2) C(Q, z_1, z_2)
\]

(17)

where \( C(Q, z_1, z_2) \) is the Fourier transform of the Ornstein–Zernike correlation function (cf Evans 1981).

The second and third terms on the rhs of equation (16) can also be easily calculated. They contribute to the tensor \( C_{\alpha \beta, \alpha' \beta'} \) terms of the form \( 2 \gamma_{\text{VDW}} (\delta_{\alpha \alpha'} \delta_{\beta \beta'} + \delta_{\alpha \beta'} \delta_{\alpha' \beta}) \). The fourth term on the rhs of equation (14) is more complicated. It actually contributes only to the coefficients \( C_{13,13} \) and \( C_{23,23} \) and shows the role of the gravitational field. Indeed, using equation (15) we obtain:

\[
\int \int_{-\infty}^{\infty} d z_1 \ d z_2 [C_{13,13}(Q, z_1, z_2) + C_{23,23}(Q, z_1, z_2)]
\]

\[
= C_{13}(Q) = \gamma_{\text{VDW}}[1^2 Q_j^2 / (1 + l^2 Q_j^2)].
\]

(18)

The expression (18) shows that one should first take \( g \to 0 \) limit and only then let \( Q \to 0 \). In that limit one gets, as expected, \( C_{13} = \gamma_{\text{VDW}} \).

The contribution to \( C_{33,33} \) can also be calculated in this limit and that turns out to be equal to \( 2 \gamma_{\text{VDW}} \). Collecting back all the terms we can write down the tensor \( \tilde{C}_{\alpha \beta, \alpha' \beta'} \) as:

\[
\tilde{C}_{\alpha \beta, \alpha' \beta'} = \kappa \delta_{\alpha \alpha'} \delta_{\beta \beta'} + 2 \gamma_{\text{VDW}} (\delta_{\alpha \alpha'} \delta_{\beta \beta'} + \delta_{\alpha \beta'} \delta_{\alpha' \beta})
\]

\[
+ \gamma_{\text{VDW}} (\delta_{\alpha \delta} \delta_{\beta \gamma} \delta_{\beta' \delta'} + \delta_{\alpha \delta} \delta_{\beta' \delta'} \delta_{\beta \gamma}).
\]

(19)

One can also rewrite equation (19) using the Voigt notation customary in elasticity theory. The non-vanishing components of \( \tilde{C}_{AB} \) \( (A = B = 1, \ldots, 6 \text{ with } 1 = (11), 2 = (22), \ldots, 6 = (23)) \) are then:

\[
\tilde{C}_{11} = \tilde{C}_{22} = \tilde{C}_{zz} = \kappa \quad \tilde{C}_{33} = \kappa + 6 \gamma_{\text{VDW}}
\]

(20)

\[
\tilde{C}_{12} = \kappa + 2 \gamma_{\text{VDW}} = \tilde{C}_{23} \quad \tilde{C}_{55} = \tilde{C}_{66} = \gamma_{\text{VDW}}.
\]

Note that the number of independent elastic moduli \( \tilde{C}_{AB} \) is now equal to four, precisely for the same reason as in the case of a homogeneous fluid where the field-theoretical model gives only one coefficient, namely (15).

Subtracting from the moduli (20) the Gibbs construction values of \( C_{AB} \), which we shall put equal to the single-phase value, one obtains the elastic coefficients of the interface \( E_{AB} \). They differ from (20) in replacing \( \kappa \) by \( \kappa - k_{\text{hom}} \). One expects that this difference is very small, particularly close to \( T_c \).

In order to illuminate the physical meaning of our expressions we calculate, following Baus (1982), the linear combinations of \( \tilde{C}_{AB} \) which are conventionally called simple shear \(-G'\), pure shear \(-G^0\), stretch \(-S\) and squeeze \(-Q\) moduli. For a homogeneous fluid within our model all these moduli vanish. Thus it is the broken rotational and translational symmetry of the system with an interface that gives rise to non-vanishing shear moduli. The squeeze modulus \( Q \) should then be identical to the conventionally defined surface tension.

Using the Voigt notation the simple shear modulus is

\[
G' = \gamma \left( \tilde{E}_{11} + \tilde{E}_{22} + \tilde{E}_{33} - \tilde{E}_{12} - \tilde{E}_{13} - \tilde{E}_{23} \right) = \gamma_{\text{VDW}}
\]

(21)
the pure shear modulus $G''$ is

$$G'' = \frac{1}{2}(E_{15} + E_{65}) = \frac{1}{2} \gamma_{VDW}$$

(22)

the stretch modulus $S$ is

$$S = \frac{1}{2} \sum_{i=1}^{3} (2E_{ij} - E_{ii}) = \frac{1}{2} \gamma_{VDW}$$

(23)

and finally the squeeze modulus $Q$ is

$$Q = E_{23} - E_{21} - E_{63} = \gamma_{VDW}$$

(24)

as expected.

One sees from expressions (21)-(24) that all the moduli are given in terms of the only stiffness coefficient for the interface, that is $\gamma_{VDW}$.

We have shown therefore that the high-frequency response of the liquid–vapour interface can be analysed within the continuous or field-theoretical model and that one obtains explicit expressions for the elastic moduli. The values of these moduli, apart from the squeeze modulus, cannot be directly compared with those calculated by Bausch since, as mentioned above, the continuous model does not account properly for transverse reaction of the homogeneous fluid. On the other hand this model seems to be applicable to the study of an interface between solid and superfluid helium.

As already mentioned, the isotropic dominant part of the dispersion relation for crystallisation waves (Andreev 1982) is identical to the dispersion relation for ‘isothermal capillary waves’ as obtained by Turski and Langer (1980). We anticipate, therefore, that the high-frequency response of the quantum-solid–superfluid-liquid interface should exhibit not only the crystallisation waves but three other propagating modes, ‘spring’ constants of which will be related to these additional elastic moduli of the interface we have discussed in this paper. The experimental observation of high-frequency modes propagating on the liquid–vapour interface close to $T_c$ seems to be extremely difficult but not entirely ruled out.

Acknowledgments

One of us (LAT) would like to thank Richard Bausch, Michel Droz, Charles Enz, Heiner Müller-Krumbhaar and Herbert Wagner for interesting discussions on interfaces. Financial support of the IPP-KFA Jülich and warm hospitality of Professor H Müller-Krumbhaar’s group extended to LAT is sincerely acknowledged.

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