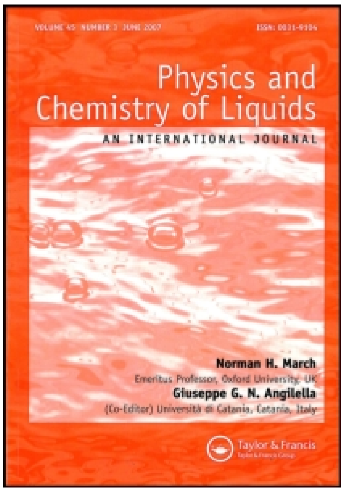

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GRAVITATIONAL FIELD EFFECTS ON MEMBRANE EQUILIBRIUM, DISTENDED WATER AND THE LIQUID–VAPOUR INTERFACE

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Motivated by the rise of sap in coastal redwood trees, the statistical mechanics of inhomogeneous fluids is set out in a form appropriate to discuss (a) a liquid–vapour interface formed in pure water under gravity and (b) an aqueous solution containing a non-volatile solute such as glucose in which water is in equilibrium through a semipermeable membrane with distended pure water. In principle, low-order gradient expansions allow the density profiles of both pure water and the two-component fluid to be calculated in a gravity field.

KEY WORDS: Osmosis, Hulett's theory, distended solvent, membrane equilibrium, density profiles.

1 INTRODUCTION

Early experiments by one of us[1], in which the behavior at the top of the column of water in coastal redwood trees was studied, coupled with some interesting ideas of Hulett[2], have prompted us to pose the theory of pure fluids and binary fluid mixtures in a gravitational field in the form presented below. It has been clear for some time that presently tractable theories of, specifically, the liquid–vapour interface in a gravitational field, will need to invoke low-order density gradient expansions which, in fact, go back to van der Waals.

As illustrative of the approach adopted below, the flat liquid–vapour interface in the x–y plane, with number density profile $\rho(z)$, has been studied by Bhatia and March[3] in zero gravity, in order to understand further the empirical correlation between liquid surface tension σ and bulk isothermal compressibility κ_T, namely,

$$\sigma \kappa_T \approx \ell \tag{1}$$

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where the length l is the order of 1 Å. The two basic equations these workers employed expressed respectively the constancy of the chemical potential μ and the pressure p through the interface. These equations take the form[3]

$$\mu = \mu[\rho(z)] - A[\rho(z)]\rho''(z) - \tfrac{1}{2}A'[\rho(z)]\rho'(z)^2 \tag{2}$$

and

$$p = \mu[\rho(z)] - \psi[\rho(z)] + \tfrac{1}{2}A[\rho(z)]\rho'(z)^2 \colon \mu(\rho) = \partial\psi(\rho)/\partial\rho. \tag{3}$$

In these equations, it is to be determined that $\mu[\rho(z)]$ is the chemical potential of the homogeneous bulk fluid, with density $\rho(z)$. Also A is determined solely by a structure factor $c(r, \rho)$ of the bulk fluid, c being the Ornstein–Zernike direct correlation function. Specifically A is given in terms of c by

$$6A(\rho)/k_BT = \int d\mathbf{r}\, c(\mathbf{r}, \rho)r^2. \tag{4}$$

Without solving the Euler Eq. (2) for the density profile, Bhatia and March[3] were able to approximately calculate the surface tension from the van der Waals-like formula, and to regain the empirical correlation (1).

All the above is in the absence of a gravitational field. Below, this treatment will be generalized to include such an external field, following Fleming, *et al.*[4] However, before doing so, let us turn in the following section to the motivation for the present study, following the ideas of Hulett and one of us[5].

2 MOTIVATION; MEMBRANE EQUILIBRIUM AND DISTENDED PURE WATER

In this section, the motivtion for the present study will be discussed. In the right-hand part A of Figure 1, a schematic representation is given of the liquid–vapour interface formed at h under gravity. The equations describing this interface, with density profile $\rho_0(z)$, will be given in Section 3.

The middle part B of Figure 1 is motivated by the experiments on the water column in a coastal redwood tree. One can think of this as a distended column of liquid water, held in place by constraints as is the water within the xylem vessels and in the cellulose, hemi-cellulose and lignin matrix constituting the cell walls of the border parenchyma and spongy mesophyll of redwood leaves. Thus, one could think of this column of water in the middle part of the figure as being related to the right-hand picture through the liquid in B being under an additional external potential, $U(z)$ say, attributable to the weight of the liquid water below the liquid–vapour interface which is held at h' by a porous matrix.

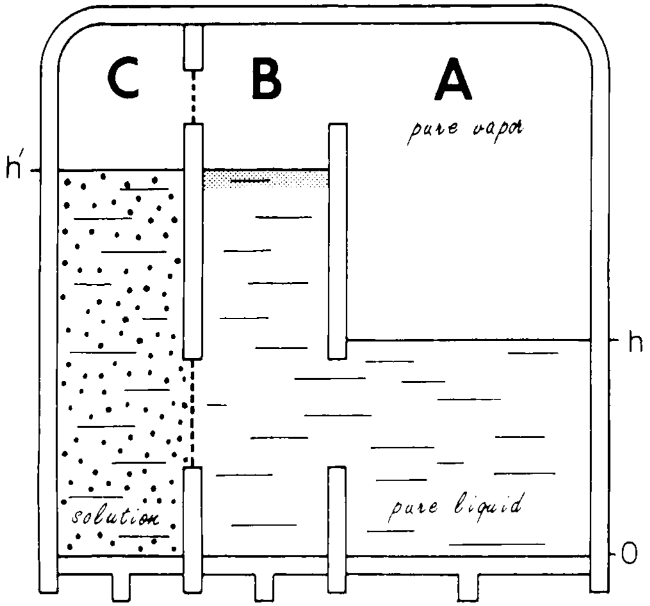

Figure 1 A. Denotes liquid-vapour interface at position h under gravitational field (for pure water). B. Denotes new position h' of liquid-vapour interface, when distended pure water (as in a redwood tree) is considered. C. Denotes an aqueous solution, with liquid-vapour interface arranged at same height h' as distended water column in B, this being achieved by equilibrium of water across the membrane at one specific solute (e.g. glucose) concentration.

The left-hand part of Figure 1, denoted by C, considers, following the ideas of Hulett, equilibrium at every z between liquid water in B and C. Water in column C is separated from water in B by a membrane permeable only to water. In addition to water in C (type 1, say, molecules) there are solute molecules of type 2 (think of glucose in water as an example); but no chemical reactions are allowed in the 'thought' experiments presented in Figure 1.

This Figure then provides the motivation for Sections 3–5 below. But the striking points that need making at this stage with regard to the density profiles we intend to use to describe these inhomogeneous fluids and fluid mixtures are as follows:

(i) In all three parts of Figure 1, the water density profile will become asymptotically the same, once one reaches heights $z \geq h'$ in the vapour phase in all three cases.

(ii) According to Hulett[2,5], in the membrane equilibrium, the water density profiles will be the same in both B and C, though not, of course, for the free liquid-vapour interface in A, formed under gravity alone.

What is remarkable about Hulett's claim is that one can, according to his contentions, arrange precisely the same profile at each height z for the water in parts B and C. Though our work does not enable us to prove Hulett's assertions, what will be demonstrated from the study of binary mixtures in a gravitational field in Section 5 is that the effect of the solute 2 on the water density profile can indeed be represented through a one-component theory in an appropriately constructed external potential. This is a vindication of the philosophy expounded by Hulett who deduced, as did one of us[5], that the solute altered the water in column C as if it was under the same tension or pressure at every z in the range $0 < z < h'$ as is the water in column B at the same z. Deductions from our analysis are less strong than Hulett's deduction as to the complete identity of the two profiles in the apparently very different physical conditions in parts B and C of Figure 1. This is the point to turn to the modifications of Eqs (2) and (3) above in the case of a free liquid-vapour interface formed under gravity.

3 LIQUID-VAPOUR INTERFACE UNDER GRAVITY

As discussed at some length by Fleming, *et al.*[4], with inclusion of the gravitational field, Eqs (2) and (3) are to be generalized to read

$$\mu + GMm/R_0 - mgz = \mu[\rho(z)] - A[\rho(z)]\rho''(z) - \tfrac{1}{2}A'[\rho(z)]\rho'(z)^2. \qquad (5)$$

Here G is the gravitational constant, g the acceleration due to gravity, M the mass of the Earth while m is the molecular mass. R_0 in Eq. (5) is the distance of some reference point, taken below to be the Gibbs surface in each case, from the center of the Earth. Equation (5) is to be solved for the density profile $\rho(z)$, which for a sufficiently large z, must asymptotically approach the Boltzmann form with a factor $\exp(-mgz/k_B T)$.

Though closely related to the change of μ from the form of Eq. (2) to Eq. (5), it is important here to emphasize that Eq. (3), which expresses the constancy of the pressure p across the inhomogeneous liquid-vapour interface must be generalized by writing the condition of mechanical equilibrium in which the 'internal force' $dp(z)/dz$ is balanced by the 'external force': i.e. gravity in the present example. Thus, one can write

$$dp(z) + m\rho(z)g\,dz = 0 \qquad (6)$$

or, by integration, the pressure difference $p(z) - p(z_0)$ between points z_0 and $z > z_0$ is found to be

$$p(z) + m\int_{z_0}^{z} dz\rho(z)g = p(0). \qquad (7)$$

This can be regarded as a statement of Bernoulli's Theorem, and its content is that the pressure at height z relative to that at z_0 is diminished by the total weight per unit area of fluid between the points z_0 and z. One can add to Eqs (5)-(7) a further equation which reduces to the usual surface tension σ in the limit $g \to 0$. Of course, in the presence of gravity, even the liquid phase is (slightly) inhomogeneous and this leads to a density gradient contribution to the 'tension' away from the surface region. But in general such a correction to the surface tension is a minor one, and will not be considered further here.

4 LIQUID-VAPOUR INTERFACE IN DISTENDED WATER

One must add to the previous Eq. (5) the effect of a 'matrix', or a constraint, which holds column B of Figure 1 at the appropriate height shown. If it is possible to represent such a constraint by suitable boundary conditions, then one would merely have to solve Eq. (5) with different R_0 and different boundary conditions to obtain $\rho_1(z)$ for the distended water column. Otherwise, it would be necessary to add a spatially dependent 'external' potential $U(z)$ (compare the discussion of mixtures in an applied potential in the Appendix). Note that with such a potential included, one would need to modify the equations of mechanical equilibrium expressed in Eqs (6) and (7) above, again as in the Appendix dealing with inhomogeneous fluid mixtures.

5 BINARY LIQUID MIXTURES AND MEMBRANE EQUILIBRIUM

Bhatia and March[6] have developed a theory of surface segregation in a binary liquid mixture in zero gravitational field which generalizes Eq. (1) to a two-component system. Subsequently, the relation of their phenomenological theory to the multicomponent low-order density gradient method of Fleming, Yang and Gibbs[7] has been exposed by Bhatia, March and Sutton[8]. Following the presentation of these latter workers, the free energy density $\psi(z)$ for a binary liquid mixture can be expanded to lowest order in the density gradients as

$$\psi(z) = \psi[\rho_1(z), \rho_2(z)] + \frac{1}{2}\sum_{i,j} A_{ij}[\rho_1(z), \rho_2(z)]\rho_i'(z)\rho_j'(z). \tag{8}$$

Here $\rho_1(z)$ and $\rho_2(z)$ evidently represent the number density profiles in the inhomogeneous liquid mixture of components 1 and 2. The first term in Eq. (8) is the local density approximation, while the correction terms account in lowest order for any inhomogeneity in the mixture.

Introducing Lagrange multipliers μ_1 and μ_2 in the usual way, the Euler equations of the variation problem posed by Eq. (8) are

$$\mu_1 = \mu_1[\rho_1(z), \rho_2(z)] + F_1 \tag{9}$$

and

$$\mu_2 = \mu_2[\rho_1(z), \rho_2(z)] + F_2 \tag{10}$$

with

$$\mu_1[\rho_1(z), \rho_2(z)] = \partial\psi[\rho_1(z), \rho_2(z)]/\partial\rho_1(z), \tag{11}$$

$$\begin{aligned} F_1 = {} & (\rho_1')^2(-\tfrac{1}{2}\partial A_{11}/\partial\rho_1) - \rho_1'\rho_2'\partial A_{11}/\partial\rho_2 + (\rho_2')^2(\tfrac{1}{2}\partial A_{22}/\partial\rho_1 - \partial A_{12}/\partial\rho_2) \\ & - (\rho_1'' A_{11} + \rho_2'' A_{12}) \end{aligned} \tag{12}$$

and

$$\begin{aligned} F_2 = {} & (\rho_1')^2(\tfrac{1}{2}\partial A_{11}/\partial\rho_2 - \partial A_{12}/\partial\rho_1) - \rho_1'\rho_2'\partial A_{22}/\partial\rho_1 - \tfrac{1}{2}(\rho_2')^2\partial A_{22}/\partial\rho_2 \\ & - (\rho_1'' A_{12} + \rho_2'' A_{22}). \end{aligned} \tag{13}$$

Following the work of Fleming, Yang and Gibbs on the one-component case, it is noted in Ref. 8 that the surface tension of the mixture is given by

$$\sigma = \int \left[\sum_{i,j} A_{ij} \rho_i'(z) \rho_j'(z) \right] dz. \tag{14}$$

Employing the Euler equations and introducing the equilibrium pressure p, this can be expressed[3,8] in the more useful form for making contact with Eq. (1) above:

$$\sigma = 2 \int \{ p - \mu_1 \rho_1(z) - \mu_2 \rho_2(z) + \psi[\rho_1(z), \rho_2(z)] \} dz. \tag{15}$$

Without introducing further assumptions, or models, the above equations represent the furthest point along the gradient expansion route that one can reach. However, the work of Hulett[2] suggests that one should now regard the basic problem as that of describing the water (say component 1) density profile through a one-component-like theory as in Sections 3 and 4. This necessitates a relatively straight forward extension of the above equations to incorporate an external potential, which has already been considered by Fleming, Yang and Gibbs[7].

5.1 *Introduction of External Potentials*

The above treatment was appropriate to zero gravitational field. Let us now generalize this to include external potentials $U_i(z)$ which act differentially on the two components $i = 1$ and 2. Then Eq. (8) has to be modified to read

$$\psi_u(z) = \psi(z) + \sum_{i=1,2} U_i(z) \rho_i(z). \tag{16}$$

Then the chemical potential equations become as in the above equations, with $\mu_i \rightarrow \mu_i - U_i(z)$.

Following the treatment of Fleming, Yang and Gibbs[7] (see especially their Appendix A), it is useful to define a dimensionless one-body potential:

$$u_i(z) = [k_B T]^{-1} [\mu_i - U_i(z)] \equiv \beta[\mu_i - U_i(z)] \tag{17}$$

Then, in Ref. 7 the density profiles are expressed in the form

$$\rho_i(z) = \exp[u_i(z) + C_i(z)] / \lambda_i^3 \tag{18}$$

where $\lambda_i = (\beta h^2 / 2 m_i \pi)^{1/2}$ is the thermal wavelength of the ith species. Note here that $C_i(z)$ can be viewed as treating the effects of the interaction in the mixture in terms of a one-body potential seen by the ith species. Fleming, Yang and Gibbs[7] assume the 'internal' part of this one-body potential, namely $C_i(z)$, to be a functional of the densities $\rho_i(z)$.

We are interested here (see Figure 1) in the water density profile [say $\rho_1(z)$]. Using the work of Ref. 7, one can then express the 'internal' potential $C_1(z)$, which clearly must tend to zero as the densities $\rho_1(z)$ and $\rho_2(z)$ become sufficiently dilute in component 2, since the effects of interaction tend to zero at such low densities, in the (somewhat complex) form

$$C_1(z) = C_1^{\mathrm{local}}(z) + \beta[A_{11}\rho_1'' + A_{12}\rho_2'']$$
$$+ \beta \sum_{j,k} \left[\frac{\partial A_{1j}}{\partial \rho_2} - \frac{1}{2} \frac{\partial A_{2k}}{\partial \rho_1} \right] \rho_j'(z)\rho_k'(z). \qquad (19)$$

For the present study, the most important conclusion is that the effect of the component 2, say glucose molecules, on the density profile $\rho_1(z)$ of the water, can be replaced by adding to the dimensionless one-body potential $u_1(z)$ in Eq. (17) an internal potential $C_1(z)$. Then the density profile $\rho_1(z)$ can again be treated by the one-component theory summarized in Section 4: of course, somewhat formally, in view of the relative complexity of $C_1(z)$ above. Nevertheless, this all serves to vindicate the philosophy of Hulett, which is the main purpose of this section of the paper.

6 RELATION TO MEMBRANE EQUILIBRIUM

This is the point to consider membrane equilibrium between parts B and C of Figure 1. Assuming the membrane is permeable only to water, we must equate chemical potentials of species 1 in each vessel. Then we can write, with superscript zero on A_{ij} indicating zero solute concentration and with the additional assumption (cf. Hulett's ideas) that the water density profiles are the same in B and C of Figure 1:

$$\mu_1[\rho_1(z)] - \frac{1}{2}\rho_1'^2 \frac{\partial A_{11}^0}{\partial \rho_1} - \rho_1'' A_{11}^0 = \mu_1[\rho(z), \rho_2(z)] - \frac{1}{2}\rho_1'^2 \frac{\partial A_{11}}{\partial \rho_1} - \rho_1'\rho_2' \frac{\partial A_{11}}{\partial \rho_2}$$
$$+ (\rho_2')^2 \left(\frac{1}{2} \frac{\partial A_{22}}{\partial \rho_1} - \frac{\partial A_{12}}{\partial \rho_1} \right) - (\rho_1'' A_{11} + \rho_2'' A_{12}). \qquad (20)$$

Furthermore, we can write from the equation for the chemical potential of species 2

$$\mu_2 - \mu_2[\rho_1(z), \rho_2(z)] = (\rho_1')^2 \left(\frac{1}{2} \frac{\partial A_{11}}{\partial \rho_2} - \frac{\partial A_{12}}{\partial \rho_1} \right) - \rho_1'\rho_2' \frac{\partial A_{22}}{\partial \rho_1}$$
$$- \frac{1}{2}(\rho_2')^2 \frac{\partial A_{22}}{\partial \rho_2} - (\rho_1'' A_{12} + \rho_2'' A_{22}). \qquad (21)$$

This further equation can now be used to eliminate the term $\partial A_{22}/\partial \rho_1$ from Eq. (20), though A_{22} itself is thereby introduced, as well as $\partial A_{22}/\partial \rho_2$. The resulting equation would, at least in principle, allow the profile $\rho_2(z)$ to be calculated, given $\rho_1(z)$ and bulk properties of the solution alone.

Another way of viewing Eq. (20) is to say that given the density profiles $\rho_1(z)$ and $\rho_2(z)$, one of which we have seen to be determined within the above framework by pure, but distended water, Eq. (20) provides a relation at each z between properties $A_{11}^0(\rho)$ of pure water and the quantities A_{ij} of the solution. However, it must be noted that while the A_{ij}'s are determined by the two-body partial Orstein-Zernike functions at any chosen thermodynamic state, density derivatives of these relate to three-particle correlations.

It seems to us possible that the above procedure could be worked out fully within the model of conformal (closely related to regular) solution theory, where the bulk structural properties are well established from the work of Parrinello, Tori and March[9], and we are currently exploring this avenue.

7 DISCUSSION AND SUMMARY

The low-order density gradient expansion, within the framework of the statistical mechanics of inhomogeneous fluids, has been shown to be sufficient to describe the chemical physics embodied in each of the parts A, B and C of Figure 1. The liquid-vapour interface formed in a gravitational field (part A of Figure 1) could now be worked out (numerically) for a simple fluid like argon, given the Ornstein-Zernike function $c(r, \rho)$ of the bulk liquid through the entire range of densities from liquid to solid.

Turning next most naturally to part C of Figure 1, the Gibbs surface could be moved relative to the center of the Earth compared with that in part A of Figure 1 by varying the solute concentration. Given the bulk Orstein-Zernike functions A_{ij}, at this solute concentration, one could again calculate approximate density profiles $\rho_1(z)$ and $\rho_2(z)$ from the equations of Section 5. If now membrane equilibrium is established between parts B and C of Figure 1, then according to Hulett's idea, the distended water in B will have also a density profile $\rho_1(z)$.

The thought experiments embodied in Figure 1 clearly relate properties of a pure liquid, say water, in a suitably constructed 'external' potential including gravity to the effects of solute on solvent in a fluid mixture in the gravitational field. Just as in bulk liquid mixtures, progress has proved possible by the statistical mechanical theory by relating the mixture properties to those of a suitably chosen one component reference liquid[9,10], so we can anticipate that the procedure outlined in this work will help to simplify the treatment of inhomogeneous fluid mixtures in a gravitational field.

Hulett's idea that the solute in a solution distends the solvent may also be deduced by a simplified version of his thought experiment, Figure 2. This experiment could be conducted in a space craft wherein $g = 0$. In vessel 1 of Figure 2, pure liquid water is contained in a tube and is in equilibrium with its water vapour at a pressure p(i). In vessel 2 of Figure 2, a non-volatile solute is dissolved in water; the solution is contained in a tube and the solution is in equilibrium with water vapour at a lower vapour pressure p(ii). The temperature in vessel 1 is the same as in vessel 2. In vessel 3 of Figure 2, the same solution is contained in a tube at the same temperature as in vessel 2. Also in vessel 3, pure liquid water is contained in a tube and is constrained by a porous matrix at its interfaces with the vapour. The pure liquid water in its tube in vessel 3 is distended by tension and this tension lowers its vapour pressure to p(ii), the same as for the water in the solution. The pure water constrained in its tube in vessel 3

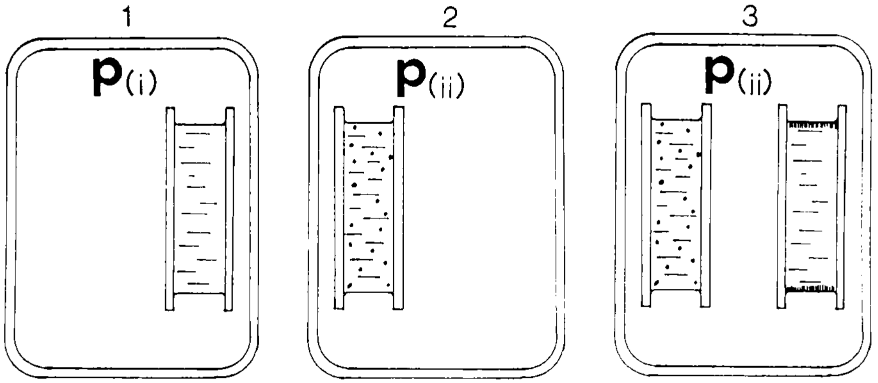

Figure 2 (1) Pure liquid water is in equilibrium with its vapour at vapour pressure p(i) in a zero gravity field. (2) Aqueous solution of a non-volatile solute is in equilibrium with water vapour at reduced vapour pressure p(ii). (3) Same solution as in (2) is in equilibrium (a) with water vapour at same pressure p(ii) and (b) with distended water, under porous constraint.

could now be coupled to the water in the solution in vessel 3 through a membrane permeable only to water and no net flow of water would result from this coupling. Again, the density profile of the constrained, distended pure liquid water mimics the density profile of the water in the solution when the fluids in both tubes are in equilibrium with the same vapour pressure at the same temperature.

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APPENDIX MECHANICAL EQUILIBRIUM IN FLUID MIXTURES

The Helmholtz free energy can, at fixed temperature, be expressed as a spatial integral of a local free energy density $\int d\mathbf{r}\psi(z)$, where in low-order density gradient expansion as employed for pure fluids in Sections 2 and 3 we can write

$$\psi(z) = \sum_{i=1,2} U_i\rho_i(z) + \psi[\rho(z)] + \frac{1}{2}\sum_{i,j} A_{ij}(\{\rho(z)\})\frac{\partial\rho_i(z)}{\partial z}\frac{\partial\rho_j(z)}{\partial z}. \tag{A1}$$

Here, $\rho_i(z)$ is the number density of species i at height z. $U_i(z)$ is an external potential as seen by species i. $A_{ij}(\{\rho\})$ is related to the molecular interaction of species i with species j. In particular,

$$A_{ij} = \frac{k_B T}{6}\int d\mathbf{r}r^2 c_{ij}(\mathbf{r}, \{\rho\}) \tag{A2}$$

where the c_{ij}'s are partial Ornstein–Zernike direction correlation functions. One obtains by minimization of the free energy, the Euler equations

$$\mu_i - U_i(z) = \mu_i(\{\rho(z)\}) - A_{ij}\rho_j''(z) - \sum_{i,j}\left[\frac{\partial A_{ij}(\{\rho(z)\})}{\partial\rho_k(z)} - \frac{1}{2}\frac{A_{ij}}{\partial\rho_i}\right]\rho_i'(z)\rho_k'(z). \tag{A3}$$

One can multiply by $\partial\rho_i/\partial z$ and sum over i to find

$$\frac{\partial\sigma_s}{\partial z} = \sum_{i=1,2}\rho_i(z)U_i'(z) \tag{A4}$$

where σ_s denotes the stress tensor. Equation (A4) is the statement that the system is mechanically in equilibrium.

For a mixture in equilibrium under gravity the previous equation for $p(z) - p(z_0)$ readily generalizes to

$$p(z) + \int_{z_0}^{z} dz m_i\rho_i(z)g = p(z_0), \tag{A5}$$

which is again Bernoulli's theorem (see also Fleming, Yang and Gibbs[7]).