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Nonuniform Classical Fluid Mixture in One-Dimensional Space with Next Neighbor Interactions

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An overcomplete description is used to represent thermodynamic potentials, for a one-dimensional classical fluid mixture with next neighbor interaction, in compact closed form. In descriptions of this class, a thermodynamic potential depends not only on minimally sufficient control variables, but on others as well with respect to which it is stationary. Here, this is done first in the direct, or fugacity-controlled format, with the grand potential as the relevant generating function. It is then transcribed to an indirect, relative density functional format, with overcompleteness restricted to a set of grand potential densities. Polydispersity requires a separate treatment. Extensions outside of the range of strict one-dimensionality are discussed, as are several approximation methods.

KEY WORDS: Classical fluid; one-dimensional; nonuniform; fluid mixture; density functional.

1. INTRODUCTION

Theoretical many-body physics, like all other scientific disciplines, is an art. The art, I would argue, is that of constructing simple solvable relevant models, whose solutions are simply expressed. This is what one needs for the coextensive purposes of understanding, extension, extrapolation, and ... fill in the blanks. But the solutions, to be truly informative, must address a broad enough context, and the minimal conditions for this purpose involve knowledge of the reaction of the system to either self-generated or

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external probes. In the realm of thermal equilibrium, our domain of choice, we need the system density "profile" in terms of an applied (static) potentials, but richer domains require more detailed information.

Coulomb forces are basic to atomic and molecular matter. At the classical level that we will adopt, they are joined by quantum mechanically generated effective forces of shorter range. Jancovici[1] has transformed the study of systems controlled by Coulomb forces through the ramifications of his exact special two-dimensional solutions. I would like to return here to perhaps analogous studies of the short-range forces that have been left behind. The immediate context will be that of one-dimensional fluids and, even more restrictive, of those with only next neighbor interactions (e.g., transmitted by the intervening medium, or with second neighbors held out of range by hard cores), but the aim will be the study of particles with internal degrees of freedom—since strict one-dimensionality as well as the next neighbor restriction can be effectively broken this way—see later.

The key concept is that of simplicity, which of course lies in the eyes of the beholder. It was found some time ago[2] that for a fluid of radius a hard rods, at reciprocal temperature β, chemical potential μ, and external potential field $u(x)$, the grand potential could be written as

$$\beta\Omega[n] = -\int \tfrac{1}{2}(n(x+a)+n(x-a))\Big/\left(1-\int_{-a}^{a} n(x+y)\,dy\right)dx, \tag{1.1}$$

where $n(x)$ is the resulting density pattern. Since Ω is related to $\bar{F}$, the intrinsic Helmholtz free energy (i.e., with external field energy $\int n(x)\,u(x)\,dx$ subtracted out)

$$\beta\Omega[n] = \left(1 - \int n(x)\frac{\delta}{\delta n(x)}\,dx\right)\beta\bar{F}[n] \tag{1.2}$$

or more simply by

$$\beta\Omega[n_\lambda] = \left(1-\lambda\frac{\partial}{\partial\lambda}\right)\beta\bar{F}[n_\lambda] \qquad \text{where} \quad n_\lambda(x) = \lambda n(x) \tag{1.3}$$

with the same relation between excess (deviation from ideal gas) quantities, $\bar{F}[n]$ can be recovered via

$$\beta F^{ex}[n] = -\int_0^1 \frac{1}{\lambda^2}\,\beta\Omega^{ex}[n_\lambda]\,d\lambda \tag{1.4}$$

or here

$$\beta F^{ex} = -\int \frac{1}{2}(n(x+a)+n(x-a)) \ln\left(1-\int_{-a}^{a} n(x+y)\, dy\right) dx. \quad (1.5)$$

Generalization to a mixture of additive hard cores of radius a_α, is not difficult,[3] and is based upon the result

$$\beta F^{ex} = -\tfrac{1}{2}\int (n^+(x)+n^-(x)) \Big/ \left[1-\int_{-\infty}^{x} (n^+(y)-n^-(y))\, dy\right] dx$$

$$\text{where} \quad n^{\pm}(x) = \sum_\alpha n_\alpha(x \pm a_\alpha) \quad (1.6)$$

A number of approximate density functionals[4] follow the form[5] of (1.1), and of course the required density profile is produced in inverse version by

$$\mu(r) = \delta \bar{F}[n]/\delta n(r) \quad (1.7)$$

equivalent to the stationary, actually minimum principle

$$\delta/\delta n(r)\left(\bar{F}[n] - \int n(r)\, \mu(r)\, dx\right) = 0; \quad (1.8)$$

here $\mu(r) = \mu - u(r)$ is the local chemical potential, that which uses the local potential as reference.

Can one extend (1.5) to larger domains of interest? There is nothing holy about the thermodynamic potential $\bar{F}[n]$, anal in fact we recall that Jancovici's 2-dimensional one-component plasma had the canonical free energy

$$F_N[u] = -\frac{1}{\beta} \operatorname{Tr} \ln \zeta^{(N)} \qquad \text{where} \quad \zeta_{jk} = \int z^j e^{-\beta u(r)} z^{*k}\, d^2r,$$

$$j, k = 0, \dots, N-1, \qquad \text{and} \qquad z = x + iy \quad (1.9)$$

a direct profile relation resulting from

$$n(r) = \delta F_N[u]/\delta u(r) \quad (1.10)$$

And the one-dimensional nearest neighbor fluid has been solved[6] in terms of the entropy functional

$$-S[n,n_2]=\int\int n_2(1,2)\ln n_2(1,2)\,d1d2-\int n(1)\ln n(1)\,d1$$
$$+\int n^R(1)\ln n^R(1)\,d1+\int n^L(1)\ln n^L(1)\,d1$$
$$+\left(1-\int n^R(1)\,d1\right)\ln\left(1-\int n^R(1)\,d1\right)$$
$$\text{where}\quad n^R(1)=n(1)-\int n_2(1,2)\,d2,$$
$$n^L(1)=n(1)-\int n_2(2,1)\,d2 \tag{1.11}$$

and $n_2(1,2)$ is the nearest neighbor pair distribution, giving rise to both spatial profile and correlations via the relations

$$\beta\mu(1)=-\delta S/\delta n(1),\qquad \beta\varphi(1,2)=\delta S/\delta n_2(1,2) \tag{1.12}$$

But the necessity of introducing 2-point conditions greatly weakens any assertion of simplicity. A theme that will color our discussion is that the use of a small number of auxiliary 1-point functions—densities of a sort—can both avoid complexity and create an instinctive physical context. We will see how these arise.

The content of this paper can be summarized as follows. In Section 2, we treat the uniform thermodynamic limit of a mixture of species with nearest neighbor interaction, in one-dimensional space. Our aim is to show how the introduction of auxiliary fields simplifies the form of the controlling grand potential, as well as to motivate the form of the corresponding non-uniform mixture grand potential, which is derived in Section 3. This expression, while simple and technically correct, depends upon a number of additional fields, and they do not appear to have direct physical significance. In Section 4, we therefore reexamine the system from the "inverse" point of view, with density rather than external field as controlling variable, a format that has produced simple closed form solutions in the past. In fact, it turns out that relative density, relative to that of the corresponding ideal gas mixture—and with excess grand potential as thermodynamic generating functional—is even more suitable, and requires only the addition of a set of grand potential densities to complete the description, Eq. (4.30). The implicit restriction to non-singular Boltzmann factor matrix is removed in Section 5, and application made to the maximally singular case of polydispersity. Finally, Section 6 indicates techniques for extending these developments to systems with one-dimensional order but not one-dimensional geometry, as well as to even less restrictive situations.

2. BULK MIXTURES

There is no dearth of techniques available to treat uniform one-dimensional fluids with next neighbor interaction, all involving an isobaric ensemble in some fashion. We will study this problem in a manner most closely related to our eventual goals. Suppose we have a fieldfree one-dimensional next neighbor interacting mixture of species indexed by $\alpha = 1,..., D$, controlled by chemical potentials $\mu_\alpha = (1/\beta) \ln z_\alpha$, and resulting in densities n_α. The ordered-particle interaction Boltzmann factors are given by

$$w_{\alpha\gamma}(x, y) = e^{-\beta\varphi_{\alpha\gamma}(y-x)}\theta(y-x) \tag{2.1}$$

where θ is the unit step function. In a grand ensemble, the particles are supplied by an external bath, so the fact that they cannot in general pass each other is irrelevant: the index of the jth particle is determined statistically. The ordered configuration $(x_1, \alpha_1), (x_2, \alpha_2)...(x_N, \alpha_N)$ in a box $[0, L]$ with fixed particles of common species α as boundaries then has the weight

$$\sum_\alpha z_{\alpha_1} \cdots z_{\alpha_N} w_{\alpha\alpha_1}(0, x_1)\, w_{\alpha_1\alpha_2}(x_1, x_2) \cdots w_{\alpha_N\alpha}(x_N, L) \tag{2.2}$$

in the grand partition function, which can then be written in index-matrix notation as

$$\Xi_L\{z_\alpha\} = \mathrm{Tr} \sum_{N=0}^{\infty} \int \cdots \int w(0, x_1)\, zw(x_1, x_2)\, z \cdots zw(x_N, L)\, dx_1 \cdots dx_N \tag{2.3}$$

Introducing the pressure p conjugate to the volume L, we find at once the grand canonical isobaric partition function

$$\begin{aligned} \Upsilon(z_1...z_D, p) &= \int_0^\infty \Xi_L\{z_\alpha\}\, e^{-\beta pL} dL \\ &= \mathrm{Tr} \sum_{N=0}^{\infty} \tilde{w}(\beta p)(z\tilde{w}(\beta p))^N \\ &= \mathrm{Tr}\, \tilde{w}(\beta p)(I - z\tilde{w}(\beta p))^{-1} \\ &\quad \text{where} \quad \tilde{w}_{\alpha\gamma}(\beta p) = \int_{-\infty}^{\infty} w_{\alpha\gamma}(0, z)\, e^{-\beta p y} dy \end{aligned} \tag{2.4}$$

Since the expected particle number is

$$\langle N \rangle = \sum z_\alpha \frac{\partial}{\partial z_\alpha} \ln \Upsilon \tag{2.5}$$

the thermodynamic limit, $\langle N \rangle \to \infty$ is equivalent to

$$I - z\tilde{w}(\beta p) \qquad \text{is singular} \tag{2.6}$$

so that $z\tilde{w}(\beta p)$ has maximum eigenvalue 1 ((2.4) would not converge if there were a larger eigenvalue). The matrix $z\tilde{w}(\beta p)$ has all positive elements, so that Perron–Frobenius theory tells us that the eigenvalue 1 belongs (to within normalization) to a unique positive right (column) eigenvector ψ, a function of βp, $\{z_\alpha\}$, and a unique positive (left) eigenvalue $\tilde{\psi}$:

$$z\tilde{w}(\beta p)\,\psi = \psi, \qquad \hat{\psi} z\tilde{w}(\beta p) = \hat{\psi} \tag{2.7}$$

At this stage, we can recall the thermodynamic relations

$$z_\gamma \partial \beta p / \partial z_\gamma = n_\gamma \tag{2.8}$$

and apply $z_\gamma \partial/\partial z_\gamma$ to the first of (2.7), $z_\alpha(\tilde{w}\psi)_\alpha = \psi_\alpha$, to obtain $z_\gamma \delta_{\alpha\gamma}(\tilde{w}\psi)_\gamma + n_\gamma z_\alpha(\tilde{w}'\psi)_\alpha + z_\alpha(\tilde{w} z_\gamma \partial\psi/\partial z_\gamma)_\alpha = z_\gamma \partial\psi_\alpha/\partial z_\gamma$, where $\tilde{w}' = \partial\tilde{w}(\beta p)/\partial\beta p$. Multiplying by $\hat{\psi}_\alpha$ and summing, $\hat{\psi}_\gamma(z\tilde{w}\psi)_\gamma + n_\gamma(\hat{\psi} z\tilde{w}'\psi) + \hat{\psi}(z\tilde{w} - I)\, z_\gamma \partial\psi/\partial z_\gamma = 0$. But from (2.7), the last term vanishes, so that

$$\hat{\psi}_\gamma(z\tilde{w}\psi)_\gamma + n_\gamma(\hat{\psi} z\tilde{w}'\psi)_\gamma = 0 \tag{2.9}$$

We are free to normalize $(\psi, \hat{\psi})$ as we wish, and shall do so as $\hat{\psi} z\tilde{w}'\psi = -1$. To this and (2.9) we append the result of applying the above operation to the second of (2.7), giving us the set

$$\begin{aligned} n_\gamma &= \hat{\psi}_\gamma (z\tilde{w}\psi)_\gamma \\ n_\gamma &= (\hat{\psi} z\tilde{w})_\gamma \psi_\gamma \qquad \hat{\psi} z\tilde{w}'\psi = -1 \end{aligned} \tag{2.10}$$

Of course, the thermodynamics of this system is completely expressed by (2.6). But (2.10) allows us to enter a format that extends almost painlessly to non-uniform fluids. It is that of constructing a multi-variable grand potential per unit volume $\Omega(\psi, \hat{\psi}, \beta p; z)$ for which, as a function of the fugacities,

$$n_\gamma = -z_\gamma\, \partial\beta\Omega/\partial z_\gamma \tag{2.11}$$

will hold but which is stationary with respect to all other variables:

$$\partial\beta\Omega/\partial\psi_\gamma = \partial\beta\Omega/\partial\hat{\psi}_\gamma = \partial\beta\Omega/\partial\beta p = 0 \tag{2.12}$$

We can write down this object at once:

$$\beta\Omega = \hat{\psi}\psi - \hat{\psi}z\tilde{w}\psi - \beta p \tag{2.13}$$

for we see that $\partial\beta\Omega/\partial\psi_\gamma = \partial\beta\Omega/\partial\psi_\gamma = 0$ reproduces (2.7) and identifies $\beta\Omega$ as $-\beta p$, which satisfies (2.6), that $\partial\beta\Omega/\partial\beta p = 0$ correctly normalizes $(\hat{\psi}, \psi)$ as in (2.10), and that (2.11) holds via the first pair, of (2.10). The advantage of the overcomplete description (2.13) with respect to the direct relationship (2.6), e.g., in the form $\mathrm{Det}(I - z\tilde{w}(\beta p)) = 0$, is that its mathematical structure is very simple. But while (2.13) is indeed brief, it is not physically transparent; this will gradually be remedied.

A standard example is worth mentioning. Suppose an additive hard rod mixture, with $\alpha\gamma$ relative core diameter of $a_\alpha + a_\gamma$; then

$$w_{\alpha\gamma}(x, y) = \theta(y - x - a_\alpha - a_\gamma)$$

$$\tilde{w}_{\alpha\gamma}(\beta p) = \frac{1}{\beta p} e^{-\beta p a_\alpha} e^{-\beta p a_\gamma} \qquad \text{and} \tag{2.14}$$

$$\beta\Omega = \sum \hat{\psi}_\alpha \psi_\alpha - \left(\sum \hat{\psi}_\alpha z_\alpha e^{-\beta p a_\alpha}\right)\left(\sum \psi_\gamma e^{-\beta p a_\gamma}\right)\Big/\beta p - \beta p$$

From (2.7) and (2.10), we have at once

$$\psi_\alpha = \frac{1}{K^{1/2}} \frac{z_\alpha e^{-\beta p a_\alpha}}{\sum z_\gamma e^{-\beta p a_\gamma}}, \qquad \hat{\psi}_\alpha = \frac{1}{K^{1/2}} \frac{e^{-\beta p a_\alpha}}{\sum e^{-\beta p a_\gamma}} \tag{2.15}$$

$$n_\alpha = \psi_\alpha \hat{\psi}_\alpha, \qquad \text{and} \qquad K = \frac{1}{\beta p} - \frac{1}{2} \frac{\sum a_\alpha e^{-\beta p a_\alpha}}{\sum e^{-\beta p a_\alpha}} - \frac{1}{2} \frac{\sum z_\alpha a_\alpha e^{-\beta p a_\alpha}}{\sum z_\alpha e^{-\beta p a_\alpha}}$$

$$\text{with} \quad \beta p = \sum z_\alpha e^{-\beta p a_\alpha}$$

3. NON-UNIFORM MIXTURE, DIRECT FORM

Our domain of interest is that of non-uniform fluid mixtures, and our immediate objective is to see how (2.13) must be extended to apply to this much richer domain.

In the presence of a spatially varying external field $u_\alpha(x)$ in the form of the local chemical potential $\mu_\alpha(x) = \mu_\alpha - u_\alpha(x)$ or relative fugacity $z_\alpha(x) = \exp \beta\mu_\alpha(x)$, the system can be contained by the potential itself without having to station boundary particles. Thus the bulk-targeted (2.3) is replaced by

$$\Xi[z] = 1 + \sum_{N=1}^{\infty} \int \cdots \int z(x_1)\, w(x_1, x_2)\, z(x_2) \cdots z(x_N)\, dx_1 \cdots dx_N \quad (3.1)$$

We will now extend the notation, so that w represents a matrix $\{w_{\alpha\gamma}(x, y)\}$ with joint discrete and continuous indices, and $z = \{z_\alpha(x)\, \delta(x-y)\, \delta_{\alpha\beta}\}$ a matrix which is diagonal on the full (α, x) space. We further define the constant vector $\mathbb{1}$:

$$\mathbb{1}_\alpha(x) = 1 \quad (3.2)$$

(and will use the same notation for vectors on any space), in which case (3.1) becomes

$$\begin{aligned} \Xi &= 1 + \mathbb{1}^T \sum_{N=1}^{\infty} (zw)^{N-1} z \mathbb{1} \\ &= 1 + \mathbb{1}^T z (1 - zw)^{-1} \mathbb{1} \end{aligned} \quad (3.3)$$

Using the general $(A^{-1})' = -A^{-1} A' A^{-1}$, the density profile is then obtained as

$$\begin{aligned} n_\alpha(x) &= \delta \ln \Xi / \delta \ln z_\alpha(x) \\ &= \mathbb{1}^T (I - zw)^{-1} (\alpha, x)\, z_\alpha(x) (\alpha, x) (I - wz)^{-1} \mathbb{1} / \Xi \\ &\equiv \Xi_\alpha^-(x)\, z_\alpha(x)\, \Xi_\alpha^+(x) / \Xi \end{aligned} \quad (3.4)$$

where

$$\Xi^+ - wz\Xi^+ = \mathbb{1}, \quad \Xi^- - \Xi^- zw = \mathbb{1}^T \quad \text{and} \quad \Xi = 1 + \mathbb{1}^T z \Xi^+ = 1 + \Xi^- z \mathbb{1} \quad (3.5)$$

Note that because $w_{\alpha\gamma}(x, y) \to 0$ as $x \to \infty$ or $y \to -\infty$, and $\to 1$ as $x \to -\infty$ or $y \to \infty$, then (3.5) implies that

$$\begin{aligned} \Xi_\alpha^+(\infty) &= \Xi_\alpha^-(-\infty) = 1 \\ \Xi_\alpha^+(-\infty) &= \Xi_\alpha^-(\infty) = \Xi \end{aligned} \quad (3.6)$$

We will return to (Ξ^+, Ξ^-) before long, but at the moment it is more convenient to define

$$\psi = z\Xi^+, \qquad \hat{\psi} = \Xi^- \quad (3.7)$$

so that

$$\begin{aligned} \psi - zw\psi &= z\mathbf{1} \\ \hat{\psi} - \hat{\psi}zw &= \mathbf{1}^T \end{aligned} \tag{3.8}$$

and among several equivalent representations, we can write, maintaining the implicit continuum indices,

$$n_\gamma = \hat{\psi}_\gamma (zw\psi + z\mathbf{1})_\gamma / \Xi \tag{3.9}$$

We now seek an "overcomplete" description $\Omega[\psi, \hat{\psi}, \Xi; z]$. The requirement $n_\gamma(x) = -\delta\beta\Omega/\delta \ln z_\gamma(x)$ is certainly met, according to (3.4), by

$$\beta\Omega' = -(\hat{\psi}zw\psi + \hat{\psi}z\mathbf{1})/\Xi \tag{3.10}$$

There is then a readily proved theorem[7] that tells us that there exists a $\Delta[\psi, \hat{\psi}, \Xi]$ such that

$$\beta\Omega = (-(\hat{\psi}zw\psi + \hat{\psi}z\mathbf{1}) + \Delta[\psi, \hat{\psi}, \Xi])/\Xi \tag{3.11}$$

both satisfies the remaining stationarity properties $\delta\Omega/\delta\psi_\alpha(x) = \delta\Omega/\delta\hat{\psi}_\alpha(x) = \delta\Omega/\delta\Xi = 0$ and reduces to the correct $\Omega[z]$ when $\psi, \hat{\psi}, \Xi$ are expressed in terms of z. The first two conditions read, taking advantage of (3.8),

$$\begin{aligned} \frac{\delta\Delta}{\delta\psi} &= \hat{\psi}zw = \hat{\psi} - \mathbf{1}^T \\ \frac{\delta\Delta}{\delta\hat{\psi}} &= zw\psi + z\mathbf{1} = \psi \end{aligned} \tag{3.12}$$

so that

$$\Delta = \hat{\psi}\psi - \mathbf{1}^T\psi + \Xi\Delta(\Xi) \tag{3.13}$$

or

$$\beta\Omega = (-\hat{\psi}zw\psi + \hat{\psi}\psi - \hat{\psi}z\mathbf{1} - \mathbf{1}^T\psi)/\Xi + \Delta(\Xi) \tag{3.14}$$

For the final condition $\partial\beta\Omega/\partial\Xi = 0$, we need $\Delta'(\Xi) = (-\hat{\psi}zw\psi + \hat{\psi}\psi - \hat{\psi}z\mathbf{1} - \mathbf{1}^T\psi)/\Xi^2 = -\mathbf{1}^T\psi/\Xi^2 = -\mathbf{1}^T z\Xi^+/\Xi^2 = (1-\Xi)/\Xi^2$, or $\Delta(\Xi) = -\ln\Xi - 1/\Xi$. We conclude, on adding a constant, that[8]

$$\beta\Omega = (-\hat{\psi}zw\psi + \hat{\psi}\psi - \hat{\psi}z\mathbf{1} - \mathbf{1}^T\psi + 1)/\Xi - 1 - \ln\Xi \tag{3.15}$$

and easily verify that this is numerically the same as $-\ln\Xi$, as must be the case.

It is instructive to reduce (3.15) to the bulk case, say in a container from $-L$ to L. This follows by setting

$$\psi(x) = \psi e^{(L-x)\beta p}, \qquad \hat{\psi}(x) = \hat{\psi} e^{(L+x)\beta p}, \qquad \Xi = e^{2\beta P l} \tag{3.16}$$

where ψ and $\hat{\psi}$ are vectors on index (species) space alone, and so (3.15) implies

$$\lim_{L \to \infty} \frac{1}{2L} \beta\Omega = -\hat{\psi} z \tilde{w}(\beta p)\, \psi + \hat{\psi}\psi - \beta p \tag{3.17}$$

which is precisely (2.13), thus verifying the asymptotic validity of (3.16).

4. INVERSE FORM, NON-SINGULAR KERNEL

a. Background

The formulation (3.15) has at least three obvious deficiencies. First is that, although we see from (3.8) and (3.9) that $n_\gamma(x) = \hat{\psi}_\gamma(x)\, \psi_\gamma(x)/\Xi$, it is not clear how to use this to reduce the overcompleteness to anything simpler. Second is that the physical significance of the nominally redundant $\hat{\psi}$, ψ is obscure, and third that while (3.15) is stationary it certainly does not represent a minimum principle, i.e., it is not convex in its independent fields. A tempting procedure is to return to Ξ^+ and Ξ^- of (3.7), producing a more symmetric formulation of (3.11),

$$\beta\Omega = [-\Xi^- z w z \Xi^+ + \Xi^- z \Xi^+ - \Xi^- z 1 - 1^T z \Xi^+]/\Xi - 1 - \ln \Xi. \tag{4.1}$$

Then mimicking the bulk case by setting ($\chi^\pm$ are still vectors in index space)

$$\Xi^-(x) = \chi^-(x)\, e^{-\int_x^\infty \beta\omega(t)\, dt}, \ \Xi^+(x) = \chi^+(x)\, e^{-\int_{-\infty}^x \beta\omega(t)\, dt}, \ \Xi = e^{-\int_{-\infty}^\infty \beta\omega(t)\, dt} \tag{4.2}$$

results in a cleaner expression

$$\begin{aligned} \beta\Omega = & -\int \chi^-(x)\, z(x)\, e^{-\int_x^y \beta\omega(t)\, dt} w(x, y)\, z(y)\, \chi^+(y)\, dx\, dy \\ & + \int \chi^-(x)\, z(x)\, \chi^+(x)\, dx - \int \chi^-(x)\, z(x)\, e^{\int_{-\infty}^x \beta\omega(t)\, dt} \\ & - \int z(x)\, e^{\int_x^\infty \beta\omega(t)\, dt} \Xi^+(x)\, dx - 1 + \int \beta\omega(t)\, dt \end{aligned} \tag{4.3}$$

But not only are the three difficulties unchanged. The additional grand potential density $\omega(t)$ is not uniquely determined: only its integral is. We should do better.

It is simplest to start afresh from (3.5), which we repeat

$$\Xi^+ - wz\Xi^+ = 1, \qquad \Xi^- - \Xi^- zw = 1^T \tag{4.4}$$

and to rewrite (3.4) as

$$\Xi_\alpha^-(x)\, \Xi_\alpha^+(x)/\Xi = \nu_\alpha(x) \qquad \text{where} \quad \nu_\alpha(x) \equiv n_\alpha(x)/z_\alpha(x) \tag{4.5}$$

Here $\nu_\alpha(x)$ can be termed the relative density of species α, that is, relative to its ideal gas value. If the $\{\nu_\alpha(x)\}$ were to serve as the basic independent variables of the fluid description, then the pair (Ξ^+, Ξ^-) could be reduced to a single field. Now $\sum \int z_\alpha(x)\, d\nu_\alpha(x)\, dx = \sum \int (\delta n_\alpha(x) - n_\alpha(x)\, \delta\beta\mu_\alpha(x))\, dx = \delta N + \delta\beta\Omega = \delta\beta\Omega^{ex}$, where Ω^{ex} is the excess grand potential, so that in this format, the profile equation will appear as

$$z_\alpha(x) = \delta\beta\Omega^{ex}/\delta\nu_\alpha(x) \tag{4.6}$$

To build a representation to take advantage of (4.5), note that since a confined system will have $\nu_\alpha(\pm\infty) = 1$, we can assure $\Xi_\alpha^+(\infty) = \Xi_\alpha^-(-\infty) = 1$ by setting

$$\begin{aligned} \Xi_\alpha^-(x) &= \nu_\alpha(x)^{1/2}\, e^{-\int_{-\infty}^{x} \beta\omega_\alpha(t)\, dt} \\ \Xi_\alpha^+(x) &= \nu_\alpha(x)^{1/2}\, e^{-\int_{x}^{\infty} \beta\omega_\alpha(t)\, dt} \end{aligned} \tag{4.7}$$

providing that we can thereafter enforce the required $\Xi_\alpha^+(-\infty) = \Xi_\alpha^-(\infty) = \Xi$ by guaranteeing that

$$\beta\Omega = -\ln \Xi = \int_{-\infty}^{\infty} \beta\omega_\alpha(t)\, dt, \qquad \text{each } \alpha \tag{4.8}$$

Then, if (4.8) holds, we can replace the second of (4.7) by the more convenient combination

$$\Xi_\alpha^+(x)/\Xi = \nu_\alpha(x)^{1/2}\, e^{-\int_{-\infty}^{x} \beta\omega_\alpha(t)\, dt} \tag{4.9}$$

The structure of the discrete-continuous matrix $\{w_{\alpha\gamma}(x, y) = w_{\alpha\gamma}(y - x)\}$ now becomes important. We know that

$$w_{\alpha\gamma}(y - x) \to \begin{cases} 1 & y - x \to \infty \\ & \text{as} \\ 0 & y - x \to -\infty \end{cases} \tag{4.10}$$

and it follows that if $\{f_\gamma(y)\}$ and $\{g_\alpha(x)\}$ are concentrated as functions, decaying sufficiently rapidly at $\pm\infty$, then

$$
\begin{aligned}
F_\alpha(x) &= (wf)_\alpha(x) \\
&= \sum_\alpha \int w_{\alpha\gamma}(y-x)\, f_\gamma(y)\, dy \to \begin{cases} 1^T f & \\ & \text{as} \\ 0 & \end{cases} \quad \begin{matrix} x \to -\infty \\ \\ x \to \infty, \end{matrix} \quad \text{all } \alpha \\
G_\alpha(y) &= (gw)_\gamma(y) \\
&= \sum_\alpha \int g_\alpha(x)\, w_{\alpha\gamma}(y-x)\, dx \to \begin{cases} g1 & \\ & \text{as} \\ 0 & \end{cases} \quad \begin{matrix} y \to \infty \\ \\ y \to -\infty \end{matrix} \quad \text{all } \gamma
\end{aligned}
\tag{4.11}
$$

Thus, w is innately singular, as an operator. However, if (4.11) comprises its full restriction of range, we can still construct a generalized inverse w^I, unique if $w^I(x, y) \to 0$ as $y \to -\infty$ is imposed, such that

$$
f = w^I F, \qquad g = G w^I \tag{4.12}
$$

satisfy (4.11) under the stated conditions on F and G. Furthermore, under the same conditions on F and G, w^I is "transferable" i.e.,

$$
\sum_\alpha \int G_\alpha(x)(w^I F)_\alpha(x)\, dx = \sum_\gamma \int (G w^I)_\gamma(y)\, F_\alpha(y)\, dy \tag{4.13}
$$

One more property will be useful, and we will obtain it in a fashion that will also be useful. If we define the two-sided Laplace transform (as in (2.4))

$$
\begin{aligned}
\tilde{w}_{\alpha\gamma}(\beta p) &= \int_{-\infty}^{\infty} w_{\alpha\gamma}(0, y)\, e^{-\beta p y}\, dy \\
\tilde{w}^I_{\alpha\gamma}(\beta p) &= \int_{-\infty}^{\infty} w^I_{\alpha\gamma}(0, y)\, e^{-\beta p y}\, dy
\end{aligned}
\tag{4.14}
$$

then from $w^I w h = h$ on concentrated h, or

$$
\iint w^I(y-x)\, w(z-y)\, h(z)\, dz\, dy = h(x) \tag{4.15}
$$

we have on taking Laplace transforms, $\tilde{w}^I(\beta p)\, \tilde{w}(\beta p)\, \tilde{h}(\beta p) = \tilde{h}(\beta p)$ so

$$
\tilde{w}^I(\beta p) = (\tilde{w}(\beta p))^{-1} \tag{4.16}
$$

Suppose we write $w_{\alpha\gamma}(0, y) = \theta(y) + f_{\alpha\gamma}(0, y)$, where

$$f_{\alpha\gamma}(x, y) = (e^{-\beta\varphi_{\alpha\gamma}(y-x)} - 1)\,\theta(y-x) \tag{4.17}$$

is the short range one-sided Mayer function of the interaction. Hence

$$\tilde{w}(\beta p) = \frac{1}{\beta p}\,\mathbb{1}\mathbb{1}^T + \tilde{f}(\beta p) \tag{4.18}$$

from which one readily verifies that

$$\tilde{w}^I(\beta p) = \tilde{f}^{-1}(\beta p) - \tilde{f}^{-1}(\beta p)\,\mathbb{1}^T\tilde{f}^{-1}(\beta p)/(\beta p + \mathbb{1}^T\tilde{f}^{-1}(\beta p)\,\mathbb{1}) \tag{4.19}$$

Since $w^I = \lim_{p\to 0}\tilde{w}^I(\beta p)\,\mathbb{1}$, it follows at once that

$$w^T\mathbb{1} = (\tilde{f}(0)^{-1} - \tilde{f}(0)^{-1}\,\mathbb{1}\mathbb{1}^T\tilde{f}(0)^{-1}/\mathbb{1}^T\tilde{f}^{-1}(0)\,\mathbb{1})\,\mathbb{1} = 0,$$
$$\text{and similarly } \mathbb{1}^T w^I = 0 \tag{4.20}$$

b. Determination of Ω^{ex}

Now we can proceed. Since $\Xi^+_\alpha(\infty) = 1$ and $\Xi^+_\alpha(-\infty) = \Xi$, independently of α, $\Xi^+ - 1$ satisfies the conditions of (4.11), so the first of (4.4) can be solved as $z\Xi^+ = w^I(\Xi^+ - \mathbb{1}) = w^I\Xi^+$, and similarly with the second of (4.4):

$$z\Xi^+ = w^I\Xi^+, \qquad \Xi^- z = \Xi^- w^I \tag{4.21}$$

Hence, from (4.5),

$$n_\alpha(x) = (\Xi^- w^I)_\alpha(x)\,\Xi^+_\alpha(x)/\Xi = \Xi^-_\alpha(x)(w^I\Xi^+/\Xi)_\alpha(x) \tag{4.22}$$

summing over α and integrating over x, we can write either of

$$N = (\Xi^- w^I)\,\Xi^+/\Xi = \Xi^-(w^I\Xi^+)/\Xi \tag{4.23}$$

That the two versions in (4.23) are the same indeed follows from $(\Xi^- w^I)\,\Xi^+ = (\Xi^- w^I)(\Xi^+ - \mathbb{1}) + (\Xi^- w^I)\,\mathbb{1} = [(\Xi^-\mathbb{1}^T)\,w^I](\Xi^+ - \mathbb{1}) + \Xi^- z\mathbb{1} = (\Xi^- - \mathbb{1}^T)[w^T(\Xi^+ - \mathbb{1})] + \Xi - 1 = \Xi^-(w^I\Xi^+) - \mathbb{1}^T w^I\Xi^+ + \Xi - 1 = \Xi^-(w^I\Xi^+) - \mathbb{1}^T z\Xi^+ + \Xi - 1 = \Xi^-(w^I\Xi^+)$. At any rate, according to the representation (4.7), we have

$$\begin{aligned} \delta\Xi^-_\alpha(x)/\delta v_\sigma(s) &= \tfrac{1}{2}\,\delta_{\alpha\sigma}\delta(x-s)\,\Xi^-_\alpha(x)/v_\sigma(s) \\ \delta(\Xi^+_\alpha(x)/\Xi)/\delta v_\sigma(s) &= \tfrac{1}{2}\,\delta_{\alpha\sigma}\delta(x-s)(\Xi^+_\alpha(x)/\Xi)/v_\sigma(x) \end{aligned} \tag{4.24}$$

and one sees, from either version in (4.23), that

$$\frac{\delta N}{\delta v_\sigma(s)} = \frac{1}{2v_\sigma(s)} [\Xi_\sigma^-(s)(w^I\Xi^+)_\sigma(s)/\Xi + (\Xi^- w^I)_\sigma(s)\,\Xi_\sigma^+(s)/\Xi] \tag{4.25}$$

By virtue of (4.22), Equation (4.25) will give the desired $\delta N/\delta v_\alpha(x) = z_\alpha(x)$ to accord with $\beta\Omega^{ex} = N + \beta\Omega(\omega)$, but which form of (4.8) is to be used to satisfy

$$\delta\beta\Omega^{ex}/\delta\beta\omega_\sigma(s) = 0 \tag{4.26}$$

is yet to be determined. We now need the analog of (4.24),

$$\begin{aligned} \delta\Xi_\alpha^-(x)/\delta\beta\omega_\sigma(s) &= -\delta_{\alpha\sigma}(x-s)\,\Xi_\alpha^-(x) \\ \delta(\Xi_\alpha^+(x)/\Xi)/\delta\beta\omega_\sigma(s) &= \delta_{\alpha\sigma}\theta(x-s)\,\Xi_\alpha^+(x)/\Xi \end{aligned} \tag{4.27}$$

Then, using the first version in (4.23),

$$\begin{aligned} \delta N/\delta\beta\omega_\sigma(s) = &-\sum_\gamma \iint \Xi_\sigma^-(x)\,\theta(x-s)\,w_{\sigma\gamma}^I(x,y)\,\Xi_\gamma^+(y)/\Xi\,dx\,dy \\ &+\sum_\alpha \iint \Xi_\alpha^-(x)\,w_{\alpha\sigma}^I(x,y)\,\theta(y-s)\,\Xi_\sigma^+(y)/\Xi\,dx\,dy \\ = &-\sum_\gamma \iint \Xi_\sigma^-(x)\,\theta(x-s)\,w_{\sigma\gamma}^I(x,y)(\Xi_\gamma^+(y)-1)/\Xi\,dx\,dy \\ &-\sum_\gamma \iint \Xi_\sigma^-(x)\,\theta(x-s)\,w_{\sigma\gamma}^I(x,y)/\Xi\,dx\,dy \\ &+\sum_\alpha \iint (\Xi_\sigma^-(x)-1)\,w_{\alpha\sigma}^I(x,y)\,\theta(y-x)\,\Xi_\gamma^+(y)/\Xi\,dx\,dy \\ = &-\sum_\gamma \int_s^\infty \int \Xi_\sigma^-(x)\,w_{\sigma\gamma}^I(x,y)\,\Xi_\gamma^+(y)/\Xi\,dx\,dy \\ &+\sum_\alpha \int_s^\infty \int \Xi_\sigma^-(x)\,w_{\alpha\sigma}^I(x,y)\,\Xi_\alpha^+(y)/\Xi\,dx\,dy \\ &-\sum_\gamma \iint_s^\infty \Xi_\sigma^-(x)\,w_{\sigma\gamma}^I(x,y)\,dx\,dy/\Xi \end{aligned}$$

or

$$\frac{\delta N}{\delta\beta\omega_\sigma(s)} = -\int_s^\infty \Xi_\sigma^-(x)(w^I\Xi^+/\Xi)_\sigma(x)\,dx$$

$$+\int_s^\infty (\Xi^- w^I)_\sigma(y)\,\Xi_\sigma^+(y)/\Xi\,dy$$

$$-\iint_s^\infty \Xi_\sigma^-(x)\,w_{\sigma\gamma}^I(x,y)\,dx\,dy/\Xi \tag{4.28}$$

But $\sum_\gamma \iint_s^\infty \Xi_\sigma^-(x)\,w_{\sigma\gamma}^I(x,y)\,dx\,dy = \lim_{p\to 0}\sum_\gamma \iint_s^\infty \Xi_\alpha^-(x)\,w_{\sigma\gamma}^I(x,y)\times e^{-\beta py}\,dx\,dy = \lim_{p\to 0}\int_s^\infty \Xi_\sigma^-(x)\,e^{-\beta px}\sum_\gamma \tilde{w}_{\sigma\gamma}^I(\beta p)\,dx = \lim_{p\to 0}\int_s^\infty \Xi_\sigma^-(x)\times \beta p e^{-\beta px}\cdot(\tilde{f}^{-1}(\beta p)\,1)_\sigma/(\beta p + 1^T\tilde{f}^{-1}(\beta p)\,1)$, in the notation of (4.18), which is just $\Xi_\sigma^-(\infty)(\tilde{f}^{-1}(0)\,1)_\sigma/1^T\tilde{f}^{-1}(0)\,1$. We therefore have

$$\delta N/\delta\beta\omega_\sigma(s) = -\int_s^\infty \Xi_\sigma^-(x)(w^I\Xi^+/\Xi)_\sigma(x)\,dx$$

$$+\int_s^\infty (\Xi^- w^I)_\sigma(y)\,\Xi_\sigma^+(y)/\Xi\,dy - \lambda_\sigma\Xi_\sigma^-(\infty)/\Xi$$

$$\text{where}\quad \lambda_\sigma = (\tilde{f}^{-1}(0)\,1)_\sigma/1^T\tilde{f}^{-1}(0)\,1 \tag{4.29}$$

which would be the same if the second version in (4.23) were used.

We expect the first two terms of (4.29) to cancel, and it follows (recalling the genesis of λ_σ) that we want to choose

$$\beta\Omega^{ex}(v,\omega) = \sum_{\alpha,\gamma}\int v_\alpha(x)^{1/2} e^{-\int_{-\infty}^x \beta\omega_\alpha(t)\,dt} w_{\alpha\gamma}^I(x,y)\, e^{\int_{-\infty}^y \beta\omega_\gamma(t)\,dt} v_\gamma(y)^{1/2}\,dx\,dy$$

$$+\sum_\sigma \int \beta\omega_\sigma(s)\,ds\,\lambda_\sigma \qquad \text{where}\quad \lambda = \lim_{\beta p\to 0}\frac{1}{\beta p}\tilde{w}(\beta p)^{-1}\,1 \tag{4.30}$$

We can then check the implied

$$z_\sigma(s) = \delta\beta\Omega^{ex}/\delta v_\sigma(s), \qquad 0 = \delta\beta\Omega^{ex}/\delta\omega_\sigma(s) \tag{4.31}$$

which become

$$z_\sigma(s) = \tfrac{1}{2} v_\sigma(s)^{-1/2} e^{-\int_{-\infty}^{s} \beta\omega_\sigma(t)\,dt} \sum_\gamma \int w^I_{\sigma\gamma}(s, y)\, e^{\int_{-\infty}^{t} \beta\omega_\gamma(t)\,dt} v_\gamma(y)^{1/2}\, dy$$

$$+ \tfrac{1}{2} v_\sigma(s)^{-1/2} \sum_\alpha \int v_\alpha(x)^1/2 e^{-\int_{-\infty}^{x} \beta\omega_\alpha(t)\,dt} w^I_{\alpha\sigma}(x, s)\, dx\, e^{-\int_{-\infty}^{s} \beta\omega_\sigma(t)\,dt} \tag{4.32}$$

and

$$0 = -\int_s^\infty \int v_\sigma(x)^{1/2} e^{-\int_{-\infty}^{x} \beta\omega_\sigma(t)\,dt} \sum_\gamma w^I_{\sigma\gamma}(x, y)\, e^{-\int_{-\infty}^{y} \beta\omega_\gamma(t)\,dt} v_\sigma(y)^{1/2}\, dx\, dy$$

$$+ \int_s^\infty \int \sum_\alpha v_\alpha(x)^{1/2} e^{-\int_{-\infty}^{x} \beta\omega_\alpha(t)\,dt} w^I_{\alpha\sigma}(x, y)\, e^{-\int_{-\infty}^{y} \beta\omega_\sigma(t)\,dt} v_\sigma(y)^{1/2}\, dx\, dy$$

$$+ \lambda_\sigma(1 - \Xi^-_\sigma(\infty)/\Xi) \tag{4.33}$$

The derivative of (4.33) with respect to s establishes the equality of the two terms in (4.32), and hence of the z-representation stemming from (4.32); then returning to (4.33), we have the required $\Xi^-_\sigma(\infty) = \Xi$, all σ.

The conciseness of our expression (4.30) can be a bit deceptive. Consider for example a 3-component Widom–Rowlinson[9] mixture, with hard core self-interaction of range 1, mutual of range 2. Here then

$$w(x, y) = \begin{pmatrix} \theta(y-x-1) & \theta(y-x-2) & \theta(y-x-2) \\ \theta(y-x-2) & \theta(y-x-1) & \theta(y-x-2) \\ \theta(y-x-2) & \theta(y-x-2) & \theta(y-x-1) \end{pmatrix} \tag{4.34}$$

If written in shorthand as

$$Dw = -E \begin{pmatrix} 1 & E & E \\ E & 1 & E \\ E & E & 1 \end{pmatrix}$$

where $D = \partial/\partial x$ and $E(x, y) = \delta(y - x - 1)$ is a displacement to the right, one finds at once that

$$w^I = \frac{1}{3}\left(\frac{1}{1-E} + \frac{2}{1+2E}\right) \begin{pmatrix} -1-E^{-1} & 1 & 1 \\ 1 & -1-E^{-1} & 1 \\ 1 & 1 & -1-E^{-1} \end{pmatrix} D \tag{4.35}$$

Since $(1-E)^{-1}(x, y)=\sum_{n=0}^{\infty} \delta(y-x-a) \rightarrow 0$ as $y \rightarrow -\infty$, this is the expanded form of w^I to use; clearly $\lambda_\sigma = 1/3$, and so (4.30) becomes

$$\begin{aligned}
\beta\Omega^{ex}(v, \omega) = &\frac{1}{3} \sum_{n=0}^{\infty} (1+(-1)^n 2^{n+1}) \\
&\times \iint \Bigg[\sum_{\alpha} v_\alpha(x)^{1/2} e^{-\int_{-\infty}^{x} \beta\omega_\alpha(t)\,dt} \sum_{n} \frac{d}{dx} (v_\gamma(x+n)^{1/2} e^{\int_{-\infty}^{x+n} \beta\omega_\gamma(t)\,dt}) \\
&-\sum_{n} v_\alpha(x)^{1/2} e^{-\int_{-\infty}^{x} \beta\omega_\alpha(t)\,dt} \frac{d}{dx} (v_\alpha(x+n)^{1/2} e^{\int_{-\infty}^{x+n} \beta\omega_\alpha(t)\,dt} \\
&+2v_\alpha(x+n-1)^{1/2} e^{-\int_{\infty}^{x+n-1} \beta\omega_\alpha(t)\,dt}) \Bigg] dx \\
&+\frac{1}{3} \sum \int \omega_\alpha(x)\,dx
\end{aligned} \tag{4.36}$$

which can be further simplified, but remains fairly complicated.

5. SINGULAR KERNEL

Eq. (4.30) is our basic result. With relative densities as control variables, the overcompleteness is confined to the introduction of a set of grand potential densities or local pressures (not necessarily with kinetic implications). Of course, concavity of Ω^{ex} is not guaranteed, and the structure of w^I can be quite involved. In fact, w^I need not even exist except as a limit and this is the situation we now attend to.

The example (1.6) of an additive radius a_α hard rod mixture, with $w_{\alpha\gamma}(x, y) = \theta(y-x-a_\alpha-a_\gamma)$, is one in which $\tilde{w}_{\alpha\gamma}(\beta p) = (1/\beta p)\, e^{-\beta p a_\alpha} e^{-\beta p a_\gamma}$ is very much non-invertible. In fact, the simplicity of (1.6) is due primarily to this aspect. To accommodate singular Boltzmann factors or kernels, let us write

$$w = w^+ w_0 w^- \tag{5.1}$$

where w^+ and w^- need not be square matrices on index space, but the small square matrix w_0 is invertible on its space in the sense that $\tilde{w}_0(\beta p)$ exists for $\beta p \neq 0$ and has an inverse $\tilde{w}_0^I(\beta p)$. We will also impose normalization in the sense that

$$\begin{aligned}
w^- \mathbb{1} = \mathbb{1}, \qquad \mathbb{1}^T w^+ = \mathbb{1}^T \\
w^+ \mathbb{1} = \mathbb{1}, \qquad \mathbb{1}^T w^- = \mathbb{1}^T
\end{aligned} \tag{5.2}$$

where $\rceil$ and $\rceil^T$ are constant, equal to 1, in their associated spaces. Nonsingular transformations on index space alone can always be inserted to guarantee (5.2), which one can show are consistent with $w_{\alpha\gamma}(y-x)|_{-\infty}^{\infty} = w_{0\alpha\gamma}(y-x)|_{-\infty}^{\infty} = 1$.

To deal with (5.1), it suffices to set up an auxiliary system

$$\begin{aligned} \Xi_0^+ &= \rceil + w_0 z_0 \Xi_0^+ \\ \Xi_0^- &= \rceil^T + \Xi_0^- z_0 w_0 \end{aligned} \tag{5.3}$$

on the index space of w_0, where

$$z_0 = w^- z w^+; \tag{5.4}$$

in general, z_0 is no longer diagonal on either index or continuum space. If we solve (5.3, 5.4) then on defining

$$\Xi^+ = w^+ \Xi_0^+, \qquad \Xi^- = \Xi_0^- w^- \tag{5.5}$$

and using (5.2), we see that

$$\begin{aligned} \Xi^+ &= \rceil + wz\Xi^+ \\ \Xi^- &= \rceil^T + \Xi^- zw \end{aligned} \tag{5.6}$$

as desired. Furthermore, we have $\Xi = 1 + \rceil^T wz\Xi^+ = 1 + \rceil^T w^+ w_0 w^- zw^+ \Xi^+$, and similarly with $\Xi = 1 + \Xi^- zw\rceil$, so that

$$\Xi = 1 + \rceil^T w_0 z_0 \Xi_0^+ = 1 + \Xi_0^- z_0 w_0 \rceil \tag{5.7}$$

In other words, the reduced space (5.3, 5.7) quite directly imply the solution of the full problem.

To take advantage of (5.3, 5.7), let us go back to an earlier stage of the extended density space development,[14] that which focuses on the intrinsic Helmholtz free energy $\bar{F}$, and perturb w so that it is no longer singular. We want to be able to reproduce (3.4) and (3.5) in the form (1.7) and with the boundary conditions (3.6):

$$\Xi^+ - wz\Xi^+ = 1, \qquad \Xi^- - \Xi^- zw = \rceil^T \tag{5.8a}$$

$$\Xi_\alpha^+(\infty) = \Xi_\alpha^-(-\infty) = 1, \qquad \Xi_\alpha^+(-\infty) = \Xi_\alpha^-(\infty) = \Xi \tag{5.8b}$$

$$z_\alpha(x) = n_\alpha(x)\, \Xi / \Xi_\alpha^-(x)\, \Xi_\alpha^+(x) \tag{5.8c}$$

$$n_\alpha(x) = \delta\bar{F}[n]/\delta n_\alpha(x) \tag{5.8d}$$

by setting up an overcomplete free energy $\bar{F}[n, \Xi^+, \Xi^-, \Xi]$ which is stationary with respect to Ξ^+, Ξ^-, Ξ. The strategy of (3.11) et seq. is appropriate. We start by writing

$$\beta\bar{F} = \sum_\alpha \int n_\alpha(x)[\ln n_\alpha(x) - 1 + \ln \Xi - \ln \Xi_\alpha^+(x) - \ln \Xi_\alpha^-(x)]\, dx \\ + \Delta[\Xi^+, \Xi^-, \Xi] \tag{5.9}$$

so that (5.8d) reproduces (5.8c), and then sequentially determine Δ by requiring first (5.8a), in the form (4.21), and then (5.8b) to be reproduced. Watching boundary values as we did in Sec. 4 it is easy to verify that

$$\beta\bar{F}[n, \Xi^+, \Xi^-, \Xi] \\ = \sum_\alpha \int n_\alpha(x)[\ln n_\alpha(x) - 1 + \ln \Xi - \ln \Xi_\alpha^-(x) - \ln \Xi_\alpha^+(x)]\, dx \\ + \frac{1}{\Xi}\Xi^- w^I \Xi^+ + \Xi^-(-\infty)\left(\Xi^+(\infty) - \frac{1}{\Xi}\Xi^+(-\infty)\right) - \ln \Xi \tag{5.10}$$

will do the trick, and that either order of application of w^I can be used. But maintaining the relations (5.1, 5.2, 5.5) for our regularized w, we have $\Xi^- w^I \Xi^+ = \Xi_0^- w^-(w^+ w_0 w^-)^I w^+ \Xi_0^+ = \Xi_0^- - w_0^I \Xi_0^+$, as well as $\Xi_\alpha^\pm(\pm\infty) = \Xi_{0\alpha}^\pm(\pm\infty)$. Thus, (5.10) translates to

$$\beta\bar{F}[n, \Xi^+, \Xi^-, \Xi] \\ = \sum_\alpha \int n_\alpha(x)[\ln n_\alpha(x) - 1 + \ln \Xi - \ln(\Xi_0^- w^-)_\alpha(x) - \ln(w^+ \Xi_0^+)_\alpha(x)]\, dx \\ + \frac{1}{\Xi}\Xi_0^- w_0^I \Xi_0^+ - \ln \Xi + \Xi_0^-(-\infty)\left(\Xi_0^+(\infty) - \frac{1}{\Xi}\Xi_0^+(-\infty)\right) \tag{5.11}$$

and we are free to take the limit as the range of w^+ and domain of w^- contract, equivalent to rows, and columns respectively, becoming zero, rendering them singular and w_0 acting on the reduced index space.

The expression (5.11) can now be manipulated to produce a form analogous to (4.30). Let us however start with the simplest version, that in which the interacting mixture is polydisperse in the sense that w on index space, or equivalently $\tilde{w}(\beta p)$, is of rank 1, so we may write

$$w_{\alpha\gamma} = w_\alpha^+ w_0 w_\gamma^- \tag{5.12}$$

each factor being a translation-invariant operator on physical space, but w^+ a column vector, w_0 a scalar, and w^- a row vector on index space. All interactions are in a way images of the basic w_0. We then follow (4.7) by setting

$$\Xi_0^-(x) = v_0(x)^{1/2}\, e^{-\int_{-\infty}^{x} \beta\omega_0(t)\, dt}$$
$$\Xi_0^+(x) = v_0(x)^{1/2}\, e^{-\int_{x}^{\infty} \beta\omega_0(t)\, dt} \tag{5.13}$$
$$\Xi = e^{-\int_{-\infty}^{\infty} \beta\omega_0(t)\, dt}$$

so that boundary conditions are automatically satisfied, and, removing the ideal gas component, conclude that

$$\beta F^{ex}[n, v_0, \omega_0] = \iint v_0(x)^{1/2}\, e^{\int_x^y \beta\omega_0(s)\, ds} w_0^I(x, y)\, v_0(y)^{1/2}\, dx\, dy + \int \beta\omega_0(s)\, ds$$
$$-\sum_\alpha \int n_\alpha(x) \bigg[\ln \int v_0(y)^{1/2}\, e^{\int_{-\infty}^{y} \beta\omega_0(s)\, ds} w_\alpha^-(y, x)\, dy$$
$$+ \ln \int w_\alpha^+(x, y)\, v_0(y)^{1/2}\, e^{\int_{-\infty}^{y} \beta\omega_0(s)\, ds}\, dy \bigg] dx \tag{5.14}$$

Note that from $\beta\mu_\alpha^{ex}(x) = \delta\beta F^{ex}/\delta n_\alpha(x)$, we now have

$$v_\alpha(x) = \int v_0(y)^{1/2}\, e^{-\int_{-\infty}^{y} \beta\omega_0(s)\, ds} w_\alpha^-(y, x)\, dy$$
$$\times \int w_\alpha^+(x, y)\, v_0(y)^{1/2}\, e^{-\int_{-\infty}^{y} \beta\omega_0(s)\, ds}\, dy \tag{5.15}$$

The additive polydisperse case is particularly simple. Here, the interactions differ only by the size of a central core:

$$w_{\alpha\gamma}(y - x) = w_0(y - x - a_\alpha - a_\gamma) \tag{5.16}$$

which implies that

$$w_\alpha^+(x, y) = w_\alpha^-(x, y) = \delta(y - x - a_\alpha) \tag{5.17}$$

reducing (5.14) to

$$\beta F^{ex}[n, v_0, \omega_0] = \iint v_0(x)^{1/2}\, e^{\int_x^y \beta\omega_0(s)\, ds} w_0^I(x, y)\, v_0(y)^{1/2}\, dx\, dy + \iint \beta\omega_0(s)\, ds$$
$$-\int n^+(x) \left(\tfrac{1}{2} \ln v_0(x) - \int_{-\infty}^{x} \beta\omega_0(s)\, ds \right) dx$$
$$-\int n^-(x) \left(\tfrac{1}{2} \ln v_0(x) + \int_{-\infty}^{x} \beta\omega_0(s)\, ds \right) dx \tag{5.18}$$

in the notation of (1.6). In principle, stationarity of (5.18) with respect to v_0 and ω_0 allows v_0 and ω_0 to be found in terms of n^+ and n^-, hence determining the strict density functional βF^{ex}. In particular, this is trivial for the pure hard core case $w_0(x, y) = \theta(y-x)$, $w_0^I(x, y) = \delta(y-x)$, where one finds at once

$$\text{pure core: } v_0(x) = 1 + \int_{-\infty}^{x} (n_-(y) - n_+(y))\, dy$$

$$w_0(x) = \tfrac{1}{2}(n_-(x) + n_+(x))/v_0(x) \tag{5.19}$$

If w is of higher rank than one, the only modification in form is that one must again impose the condition that $\beta\Omega = \int \beta\omega_\alpha(s)\, ds$ is independent of α by suitable Lagrange parameters:

$$\begin{aligned}\beta F^{ex}[n, v_0, \omega_0] = \sum_{\alpha\gamma} \iint & v_{0\alpha}(x)^{1/2} e^{-\int_{-\infty}^{x} \beta\omega_{0\alpha}(s)\, ds} \\ & \times w_{0\alpha\gamma}^{I}(x, y)\, e^{\int_{-\infty}^{y} \beta\omega_{0\gamma}(s)\, ds} v_{0\gamma}(y)^{1/2}\, dx\, dy \\ & - \sum_{\alpha} \int n_\alpha(x) \bigg[\ln \int \sum_{\alpha} v_{0\gamma}(y)^{1/2}\, e^{-\int_{-\infty}^{y} \beta\omega_{0\gamma}(s)\, ds} w_{\gamma\alpha}^{-}(y, x)\, dy \\ & + \ln \int \sum_{\gamma} w_{\alpha\gamma}^{+}(x, y)\, v_0(y)^{1/2}\, e^{-\int_{-\infty}^{y} \beta\omega_{0\gamma}(s)\, ds}\, dy \bigg] \\ & + \sum \lambda_\sigma \int \beta\omega_{0\sigma}(s)\, ds \end{aligned} \tag{5.20}$$

and exactly as in (4.29), this leads to

$$\lambda = \lim_{\beta p \to 0} \frac{1}{\beta p}\, \tilde{w}^I(\beta p)\, 1 \tag{5.21}$$

6. EXTENSIONS AND APPROXIMATIONS

Strict spatial one-dimensionality is most often an idealization. One-dimensional ordering need not be. Particles with hard cores in a sufficiently constrained channel cannot change their order, but they do have an "internal" degree of freedom, that of transverse location, say t. Under these circumstances even an isotropic interaction Boltzmann factor for a simple fluid, $w(|r-r'|)$, should be written as

$$w_{tt'}(x, x') = w([(x-x')^2 + (t-t')^2]^{1/2})\, \theta(x'-x) \tag{6.1}$$

where $r = (x, t)$, and regarded as representing a continuous index mixture. The only formal modification in our discussion is that sums, as in (4.30), must now be replaced by integrals. Of course ordering by a Cartesian coordinate may be inappropriate—for a fluid in a bent tube, the longitudinal and transverse variables should instead be taken as curvilinear coordinates.

It is possible to break the condition of strict ordering, albeit weakly, by going to one further level of complexity.[10] For example, if a channel is broad enough to allow two particles to pass each other, but not three, one can take as units successive pairs of particles, say j and $j+1$ in order, with x_j less than x_{j+1}, as the location of the pair, but $d_j = x_{j+1} - x$, t_j, and $u_j = t_{j+1}$ as internal degrees of freedom of the pair. Thus one has particles $X_j = (x_j; d_j, t_j, u_j)$, perhaps simplest with pair–pair Boltzmann factor

$$w_{dtu\, d't'u'}(x, x') = \delta(x'-x-d)\, \delta(t'-u)\, \theta(x'-x) \tag{6.2}$$

that identifies the common particles of two pairs and fugacity

$$z_{dtu}(x) = z(x)\, w([d^2 + (t-u)^2)^{1/2})\, \theta(d) \tag{6.3}$$

to pick up the full interaction, which can alternatively be included in (6.2). A very similar format applies to the case of second neighbor interaction among ordered particles.

What (6.1, 6.2, 6.3) put in evidence is a substantial increase in complexity of the thermodynamic potential that describes the system. This is hardly a disaster, since the associated variational principle allows for intelligent ansatze[11] for the fields to be inserted. There are however other approximation techniques that one should he aware of in the present context. One depends upon the observation that the rank one, or polydisperse case (5.12) very greatly reduces the computational complexity. This suggests replacing $\tilde{w}_{\alpha\gamma}(\beta p)$ by its maximal eigenvalue component, i.e., the form $\tilde{w}^+_\alpha(\beta p)(1/\beta p)\, \tilde{w}^-_\sigma(\beta p)$ as leading approximation, and then picking up additional eigenstates as correction terms. The leading approximation has characteristic deficiencies in 2-phase systems (which do exist in one dimension[12]) which will be reported at a later date.

Another suggested approximation technique is in the Galerkin class.[13] In its simplest form, we can take the single component form[14] (4.30) of $\beta\Omega^{ex}$ and use it as a model for arbitrary interactions in higher dimensional space. Modelling $w^i(x, y)\, e^{\int_x^y \beta\omega(t)\, dt}$ is hardly unique, but if one is willing to fit both a one-variable and two-variable function by using empirical distribution data for the bulk fluid, or low density expansion data, the expression

$$\beta\Omega^{ex}[\nu, \omega] = \iint \nu(x)^{1/2}\, W(y-x)\, e^{\int K(x-t,\, y-t)\, \beta\omega(t)\, dt} \nu(y)^{1/2}\, dx\, dy + \int \beta\omega(t)\, dt \tag{6.4}$$

would be suitable. Even simpler, and still consistent with its progenitor (4.30) would be the one-variable model

$$K(x-t,\, y-t) = K((x-t)\cdot(y-t)) \tag{6.5}$$

In summary, what has been accomplished is the exact representation, in assertedly physically transparent form, of a thermodynamic potential that allows one in principle to solve for the structural properties of a highly specialized but still quite large class of non-uniform classical fluids. "Technical details," such as establishment of convexity, of course remain. But more importantly, if this is to be the beginning of a useful program, the effective restriction to short range forces must be overcome, and it is the work of Jancovici that gives us hope that this can be done in a meaningful way.

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