

Local thermodynamics of inhomogeneous fluids at equilibrium

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Extensive thermodynamic parameters of inhomogeneous fluids in thermal equilibrium are expressed as integrals of corresponding locally defined quantities. In particular, the distinction between the grand canonical potential and the integrated mechanical pressure is discussed in terms of scale invariance, and a similar analysis is made of the Helmholtz free energy.

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I. INTRODUCTION

Here we present an attempt to establish a rigorous approach for the description of inhomogeneous fluids at thermal equilibrium in terms of properly defined local thermodynamic quantities. Such a theory is needed, for example, for the study of fluids near interfaces and in microporous media, (see Refs. [1] and [2]), where the pores are often in a size region 5–20 Å. Also, the latest developments in transport theory of dense, strongly inhomogeneous fluids [3–5] demonstrate that dynamical properties of such fluids can be determined in terms of the pressure tensor $P[n; \mathbf{r}]$ and “structure factors” [the number density $n(\mathbf{r})$ and direct and pair correlation functions] of such fluids at thermodynamic equilibrium. Thus one has to define a pressure tensor under inhomogeneous conditions.

As has been stressed [6], such a pressure tensor should satisfy the mechanical equilibrium condition

$$\nabla_r \cdot P[n; \mathbf{r}] = -n(\mathbf{r}) \nabla_r u(\mathbf{r}), \quad (1.1)$$

where $u(\mathbf{r})$ denotes an external potential field, ∇_r symbolizes the spatial gradient operator, and the dot \cdot means the inner product.

Though Eq. (1.1) does not define $P[n; \mathbf{r}]$ uniquely or in terms of the fluid parameters [say, $n(\mathbf{r})$ and temperature T], a general class of pressure density functionals satisfying Eq. (1.1) has been derived [7], which we will refer to in the sequel. Here we would like to concentrate on the relationship between the mechanical quantity $P[n; \mathbf{r}]$ and the thermodynamic potentials of the inhomogeneous fluids. In particular, should we expect the intuitively comfortable relation

$$\Omega[n] = - \int p[n; \mathbf{r}] d\mathbf{r} \quad (1.2)$$

Here $\Omega[n]$ is the grand canonical potential and $p[n; \mathbf{r}]$ the usual scalar pressure: $p[n; \mathbf{r}] = 1/3 \text{Tr} P[n; \mathbf{r}]$, where Tr means the trace of a tensor. As we show below, this

relation does not hold. Nevertheless, the difference between the left- and right-hand sides of Eq. (1.2) is a thermodynamic quantity independent of the particular choice of $P[n; \mathbf{r}]$, and this will lead to a relevant local description for other thermodynamic parameters of the fluid as well.

II. THERMODYNAMIC REPRESENTATION

We proceed first from a thermodynamic viewpoint. Suppose that $Q[n]$ is a thermodynamic quantity which is extensive, i.e., scales as volume when the number density is uniform. The key to a decomposition of $Q[n]$ into an integral over volume of a local Q density $q[n; \mathbf{r}]$ under homogeneous conditions,

$$Q[n] = \int q[n; \mathbf{r}] d\mathbf{r}, \quad (2.1)$$

is the insistence that the functional derivative $\delta Q[n]/\delta n(\mathbf{r})$ be a local quantity, so that a local description could make sense. It certainly would be so in the idealized example $Q[n] = \int f(n(\mathbf{r})) d\mathbf{r}$ for some function $f(n(\mathbf{r}))$. A formal way of expressing this is to require that $\delta^2 Q[n]/\delta n(\mathbf{r})\delta n(\mathbf{r}')$ be short range in $\mathbf{r} - \mathbf{r}'$, which means that

$$\int a[n; \mathbf{r}] \frac{\delta^2 Q[n] d\mathbf{r}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} \cong \int a[n; \mathbf{r}'] \frac{\delta^2 Q[n] d\mathbf{r}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}.$$

This requirement can be used at least two different ways.

The first is very formal; one simply derives from the above that whenever the inverse operator $[\int d\mathbf{r}' a[n; \mathbf{r}'] \delta/\delta n(\mathbf{r}')]^{-1}$ is well defined, then

$$Q[n] = \int d\mathbf{r} a[n; \mathbf{r}] \times \left\{ \frac{\delta}{\delta n(\mathbf{r})} \left[\int d\mathbf{r}' a[n; \mathbf{r}'] \frac{\delta}{\delta n(\mathbf{r}')} \right]^{-1} Q[n] \right\}$$

for any functional $a[n; \mathbf{r}]$ and so sets either

$$q[n; \mathbf{r}] = a[n; \mathbf{r}] \frac{\delta}{\delta n(\mathbf{r})} \left[\int d\mathbf{r}' a[n; \mathbf{r}'] \frac{\delta}{\delta n(\mathbf{r}')} \right]^{-1} Q[n] \quad (2.2)$$

or

$$q[n; \mathbf{r}] = \left[\int d\mathbf{r}' a[n; \mathbf{r}'] \frac{\delta}{\delta n(\mathbf{r}')} \right]^{-1} a[n; \mathbf{r}] \frac{\delta}{\delta n(\mathbf{r})} Q[n]. \quad (2.3)$$

Of course, in the case that $a[n; \mathbf{r}]$ is a function, Eqs. (2.2) and (2.3) become identical.

The second representation is somewhat more pictorial. One can parametrize the number density, starting at zero density to produce a path or trajectory, $n_\lambda(\mathbf{r})$, to the actual density pattern $n(\mathbf{r})$ at $\lambda=1$:

$$n_0(\mathbf{r})=0; \quad n_1(\mathbf{r})=n(\mathbf{r}). \quad (2.4)$$

Then, if $Q[n_0]=0$, one has

$$Q[n] = \int_0^1 \frac{\partial}{\partial \lambda} Q[n_\lambda] d\lambda = \int_0^1 d\lambda \int d\mathbf{r} \frac{\delta Q[n_\lambda]}{\delta n_\lambda(\mathbf{r})} \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda},$$

so one can choose

$$q[n; \mathbf{r}] = \int_0^1 d\lambda \frac{\delta Q[n_\lambda]}{\delta n_\lambda(\mathbf{r})} \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda} \quad (2.5)$$

as the Q density. If Eq. (2.5) is extended to

$$q[n_\lambda; \mathbf{r}] = \int_0^\lambda d\lambda' \frac{\delta Q[n_{\lambda'}]}{\delta n_{\lambda'}(\mathbf{r})} \frac{\partial n_{\lambda'}(\mathbf{r})}{\partial \lambda'}, \quad (2.6)$$

so that

$$\frac{\partial}{\partial \lambda} q[n_\lambda; \mathbf{r}] = \frac{\delta Q[n_\lambda]}{\delta n_\lambda(\mathbf{r})} \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda}, \quad (2.7)$$

then Eq. (2.3) is just a special case in which the trajectory is chosen so that $\partial/\partial \lambda = \int d\mathbf{r} a(\mathbf{r}) \delta/\delta n_\lambda$, and $a[n; \mathbf{r}]$ is a function $a(\mathbf{r})$.

Further consideration leads to the conclusion that any Q density for which Eq. (2.1) holds can be obtained by some particular choice of the trajectory $n_\lambda(\mathbf{r})$, so that the class of Q densities obtained via Eq. (2.5) is not restrictive. Indeed, for any $q[n; \mathbf{r}]$ which is a function of \mathbf{r} , a functional of $n(\mathbf{r})$, and satisfies Eq. (2.5), one has to find a path for which

$$q[n; \mathbf{r}] = \int_0^1 d\lambda \int d\mathbf{r}' \frac{\delta q[n_\lambda; \mathbf{r}']}{\delta n_\lambda(\mathbf{r})} \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda}. \quad (2.8)$$

Following the strategy of Eq. (2.6) this will certainly hold if

$$q_\lambda[n; \mathbf{r}] = \int_0^\lambda d\lambda' \int d\mathbf{r}' \frac{\delta q[n_{\lambda'}; \mathbf{r}']}{\delta n_{\lambda'}(\mathbf{r})} \frac{\partial n_{\lambda'}(\mathbf{r})}{\partial \lambda'}. \quad (2.9)$$

Applying $\partial/\partial \lambda$, all that is needed is

$$\frac{\partial}{\partial \lambda} q[n; \mathbf{r}] = \int d\mathbf{r}' \frac{\delta q[n_\lambda; \mathbf{r}']}{\delta n_\lambda(\mathbf{r})} \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda}, \quad (2.10)$$

or simply

$$\int d\mathbf{r}' \left\{ \frac{\delta q[n_\lambda; \mathbf{r}']}{\delta n_\lambda(\mathbf{r}')} - \int d\mathbf{r}'' \frac{\delta q[n_\lambda; \mathbf{r}'']}{\delta n_\lambda(\mathbf{r}'')} \delta(\mathbf{r}-\mathbf{r}') \right\} \frac{\partial n_\lambda(\mathbf{r}')}{\partial \lambda} = 0. \quad (2.11)$$

This equation can be solved formally (but not uniquely) for $\partial n_\lambda(\mathbf{r})/\partial \lambda$, provided the kernel is singular, which it is, because its integral with respect to \mathbf{r} vanishes. The nonuniqueness is important at the $\lambda=0$ end, because if one can be sure that $\delta q[n; \mathbf{r}]/\delta n(\mathbf{r}')=0$ at $n(\mathbf{r})=0$ (which means, for example, that Q can be the excess free energy, but not the free energy itself), then the quantity $\partial n_\lambda(\mathbf{r})/\partial \lambda$ at $\lambda=0$ can be chosen arbitrarily, and in particular so that the equation $\partial n_\lambda(\mathbf{r})/\partial \lambda = \phi[n_\lambda; \mathbf{r}]$ satisfies the second of the boundary conditions (2.4), $n_1(\mathbf{r})=n(\mathbf{r})$.

III. MECHANICAL REPRESENTATION

Since the general objective is to provide a scheme for extending the mechanics of thermal systems to small spatial scales, an alternative is to build the description out of clearly mechanical quantities, namely the pressure tensor $\mathbf{P}[n; \mathbf{r}]$. This quantity plays the dominant role and in equilibrium satisfies Eq. (1.1) of force equilibration (in nonequilibrium, the right-hand side of this equation is replaced by suitable inertial forces).

For slow spatial variations in density, $\mathbf{P}[n; \mathbf{r}]$ is isotropic, $\mathbf{P}(\mathbf{r})=p(\mathbf{r})\mathbf{I}$ (with \mathbf{I} the unit matrix), leading to the simple pressure equation

$$\nabla_r p(\mathbf{r}) + n(\mathbf{r}) \nabla_r u(\mathbf{r}) = 0,$$

where $p(\mathbf{r})$ is indeed the pressure of a local bulk fluid. If the variations are not slow, the pressure defined by the expression $p(\mathbf{r}) = \frac{1}{3} \text{Tr} \mathbf{P}(\mathbf{r})$ serves as traditional entree to a thermal description. Since the grand canonical potential takes the form $\Omega[n] = - \int d\mathbf{r} p(\mathbf{r})$ for slowly varying density, this suggests that the natural generalization of $\Omega[n]$ to arbitrary inhomogeneity is precisely Eq. (1.2).

However, Eq. (1.2) is not correct; correcting it introduces an important concept. By a trivial calculation, we observe that

$$\begin{aligned} \int d\mathbf{r} \text{Tr} \mathbf{P}[n; \mathbf{r}] &= \frac{1}{3} \int d\mathbf{r} \mathbf{P}[n; \mathbf{r}] : \nabla_r \mathbf{r} \\ &= -\frac{1}{3} \int d\mathbf{r} \mathbf{r} \nabla_r : \mathbf{P}[n; \mathbf{r}] \\ &= \frac{1}{3} \int d\mathbf{r} n(\mathbf{r}) \mathbf{r} \cdot \nabla_r \mu_{\text{in}}(\mathbf{r}), \end{aligned}$$

where

$$\mu_{\text{in}}(\mathbf{r}) = \mu - u(\mathbf{r}) \quad (3.1)$$

is the intrinsic chemical potential of the fluid.

From the above and $n(\mathbf{r}) = -\delta \Omega[n]/\delta \mu_{\text{in}}(\mathbf{r})$ one has

$$\begin{aligned}
& -\frac{1}{3} \int d\mathbf{r} \mathbf{r} \cdot \nabla_{\mathbf{r}} \mu_{\text{in}}(\mathbf{r}) \frac{\delta \Omega[n]}{\delta \mu_{\text{in}}(\mathbf{r})} \\
& = \frac{1}{3} \int d\mathbf{r} \left\{ \frac{\partial}{\partial \lambda} \mu_{\text{in}} \left[\frac{\mathbf{r}}{\lambda} \right] \right\} \bigg|_{\lambda=1} \frac{\delta \Omega[n]}{\delta \mu_{\text{in}}(\mathbf{r})} \\
& = - \left[\frac{1}{3} \lambda \frac{\partial}{\partial \lambda} \right] \Omega[\mu_{\lambda}] \bigg|_{\lambda=1}.
\end{aligned}
\tag{3.2}$$

where $\mu_{\lambda}(\mathbf{r}) = \mu_{\text{in}}(\mathbf{r}/\lambda)$.

The operation $\frac{1}{3} \lambda \partial / \partial \lambda$ is an infinitesimal scale transformation that does not alter integrals of scale-invariant quantities

Thus

$$\begin{aligned}
\frac{1}{3} \lambda \frac{\partial}{\partial \lambda} \int d\mathbf{r} f(\mu_{\lambda}(\mathbf{r})) &= \frac{1}{3} \lambda \frac{\partial}{\partial \lambda} \int d\mathbf{r} f(\mu_{\text{in}}(\mathbf{r}/\lambda)) \\
&= \frac{1}{3} \lambda \frac{\partial}{\partial \lambda} \int d\mathbf{r} \lambda^3 f(\mu_{\text{in}}(\mathbf{r})) = \lambda^3 \int d\mathbf{r} f(\mu_{\text{in}}(\mathbf{r})) \\
&= \int d\mathbf{r} f(\mu_{\text{in}}(\mathbf{r}))
\end{aligned}$$

at $\lambda=1$. Hence Eq. (1.2) is valid in any region in which $\mu(\mathbf{r})$ is changing slowly enough so that local contributions depend only on local densities and not on scale. Otherwise, Eq. (3.2) defines the grand canonical potential in terms of the pressure tensor.

The explicit characterization (3.2) in terms of $\mathbf{P}[\mu_{\text{in}}; \mathbf{r}]$ extends to other quantities as well, but its form depends upon the precise quantities being considered. For example, the intrinsic Helmholtz free energy

$$\bar{F}[n] = F[n] - \int d\mathbf{r} \mu_{\text{in}}[n; \mathbf{r}] n(\mathbf{r})$$

is a functional of the particle density rather than of the local chemical potential. Applying the same scaling here, we have

$$\begin{aligned}
\left[\frac{1}{3} \lambda \frac{\partial}{\partial \lambda} \right] \bar{F}[n_{\lambda}] \bigg|_{\lambda=1} &= \int d\mathbf{r} \frac{1}{3} \lambda \partial / \partial \lambda n(\mathbf{r}/\lambda) \frac{\delta F_{\text{in}}[n_{\lambda}]}{\delta n_{\lambda}(\mathbf{r})} \bigg|_{\lambda=1} = -\frac{1}{3} \int d\mathbf{r} [\mathbf{r} \cdot \nabla_{\mathbf{r}} n(\mathbf{r})] \mu_{\text{in}}[n; \mathbf{r}] \\
&= \frac{1}{3} \int d\mathbf{r} n(\mathbf{r}) \{ 3\mu_{\text{in}}[n; \mathbf{r}] + \mathbf{r} \cdot \nabla_{\mathbf{r}} + \mathbf{r} \cdot \nabla_{\mathbf{r}} \mu_{\text{in}}[n; \mathbf{r}] \} \\
&= \int d\mathbf{r} \mu_{\text{in}}[n; \mathbf{r}] n(\mathbf{r}) + \frac{1}{3} \int d\mathbf{r} \mathbf{r} \cdot \nabla_{\mathbf{r}} \mathbf{P}[n; \mathbf{r}]
\end{aligned}$$

or

$$\left[\frac{1}{3} \lambda \frac{\partial}{\partial \lambda} \right] \bar{F}[n_{\lambda}] \bigg|_{\lambda=1} = \int d\mathbf{r} \mu_{\text{in}}[n; \mathbf{r}] n(\mathbf{r}) - \int d\mathbf{r} \frac{1}{3} \text{Tr} \mathbf{P}[n; \mathbf{r}], \tag{3.3}$$

where $n_{\lambda}(\mathbf{r}) = n(\mathbf{r}/\lambda)$, which is the proper generalization of the homogeneous $F[n] = \mu N - \mathbf{P}V$.

For the intrinsic Gibbs free energy, $G[n] = \mu N - \int d\mathbf{r} n(\mathbf{r}) u(\mathbf{r})$, one has

$$\bar{G}[n] = \int d\mathbf{r} n(\mathbf{r}) \mu_{\text{in}}[n; \mathbf{r}], \tag{3.4}$$

already in local form.

Other extensive thermodynamic parameters are readily obtained by operations on Eqs. (3.2) and (3.3). For example, from the standard $S[\mu_{\text{in}}]/k_B = \beta^2 \delta \Omega[\mu_{\text{in}}] / \delta \beta|_{\mu, V}$ for the entropy (where $\beta = 1/[k_B T]$ and k_B is the Boltzmann constant), one at once derives:

$$\left[\frac{1}{3} \lambda \frac{\partial}{\partial \lambda} \right] \frac{1}{k_B} S[\mu_{\text{in}}] \bigg|_{\lambda=1} = -\frac{\beta^2}{3} \int d\mathbf{r} \text{Tr} \left\{ \frac{\partial \mathbf{P}[\mu_{\text{in}}; \mathbf{r}]}{\partial \beta} \right\}, \tag{3.5}$$

where $\mu_{\lambda}(\mathbf{r}) = \mu(\mathbf{r}/\lambda)$. For the residual enthalpy $H[\mu_{\text{in}}] = \Omega[\mu_{\text{in}}] + S[\mu_{\text{in}}]/k_B$, one has

$$\left[\frac{1}{3} \lambda \frac{\partial}{\partial \lambda} \right] H[\mu_{\text{in}}] \bigg|_{\lambda=1} = -\frac{1}{3} \int d\mathbf{r} \text{Tr} \frac{\partial}{\partial \beta} \{ \beta \mathbf{P}[\mu_{\text{in}}; \mathbf{r}] \}. \tag{3.6}$$

Using a particular form of the pressure tensor from Ref. [7],

$$P[n; \mathbf{r}] = \{n(\mathbf{r})\mu_{\text{in}}[n; \mathbf{r}] - f[n; \mathbf{r}]\}I + \int d\mathbf{r}_3 \int_0^1 d\gamma \frac{\delta f[n; \mathbf{r} + \gamma\mathbf{r}_3 - \mathbf{r}_3]}{\delta n(\mathbf{r} + \gamma\mathbf{r}_3)} \mathbf{r}_3 \cdot \nabla_{\mathbf{r}} n(\mathbf{r} + \gamma\mathbf{r}_3), \quad (3.7)$$

where $F[n] = \int d\mathbf{r} f[n; \mathbf{r}]$ and $f[n; \mathbf{r}] = \int_0^1 d\lambda \mu_{\text{in}}[n; \mathbf{r}] \partial n_{\lambda}(\mathbf{r}) / \partial \lambda$, this route leads to some useful explicit expressions for "localities" $\omega[n; \mathbf{r}]$ and $s[n; \mathbf{r}]$ of the grand canonical potential $\Omega[n] = \int d\mathbf{r} \omega[n; \mathbf{r}]$ and the entropy $S[n] = \int d\mathbf{r} s[n; \mathbf{r}]$, respectively;

$$\begin{aligned} \omega[n; \mathbf{r}] &= -p[n; \mathbf{r}] + \frac{1}{3} \int d\mathbf{r}' \int_0^1 d\gamma \frac{\delta f[n; \mathbf{r} + \gamma\mathbf{r}' - \mathbf{r}']}{\delta n(\mathbf{r} + \gamma\mathbf{r}')} \mathbf{r}' \cdot \nabla_{\mathbf{r}} n(\mathbf{r} + \gamma\mathbf{r}') \\ &= -p[n; \mathbf{r}] - \frac{1}{3\beta} \int d\mathbf{r}' \int_0^1 d\gamma \gamma \mathbf{r}'' \cdot \nabla_{\mathbf{r}} n(\mathbf{r} + \gamma\mathbf{r}') \int_0^1 d\lambda c_2[n_{\lambda}; \mathbf{r} + \gamma\mathbf{r}' - \mathbf{r}', \mathbf{r} + \gamma\mathbf{r}'] \frac{\partial n_{\lambda}(\mathbf{r} + \gamma\mathbf{r}')}{\partial n(\mathbf{r} + \gamma\mathbf{r}')} \frac{\partial n_{\lambda}(\mathbf{r} + \gamma\mathbf{r}' - \mathbf{r}')}{\partial \lambda}, \end{aligned} \quad (3.8)$$

$$\begin{aligned} s[n; \mathbf{r}] &= k_B \beta^2 \left\{ - \left[\frac{\partial p[n; \mathbf{r}]}{\partial \beta} \right]_{\mu, \nu} + \frac{1}{3} \int d\mathbf{r}' \int_0^1 d\gamma \int d\mathbf{r}'' \frac{\delta^2 f[n; \mathbf{r} + \gamma\mathbf{r}' - \mathbf{r}']}{\delta n(\mathbf{r} + \gamma\mathbf{r}') \delta n(\mathbf{r}'')} \left[\frac{\partial n(\mathbf{r}'')}{\partial \beta} \right]_{\mu, \nu} \mathbf{r}' \cdot \nabla_{\mathbf{r}} n(\mathbf{r} + \gamma\mathbf{r}') \right. \\ &\quad \left. + \frac{1}{3} \int d\mathbf{r}' \int_0^1 d\gamma \frac{\delta f[n; \mathbf{r} + \gamma\mathbf{r}' - \mathbf{r}']}{\delta n(\mathbf{r} + \mathbf{r}')} \mathbf{r}' \cdot \nabla_{\mathbf{r}} \left[\frac{\partial n(\mathbf{r} + \gamma\mathbf{r}')}{\partial \beta} \right]_{\mu, \nu} \right\}. \end{aligned} \quad (3.9)$$

where $c_2[n_{\lambda}; \mathbf{r} + \gamma\mathbf{r}' - \mathbf{r}', \mathbf{r} + \gamma\mathbf{r}']$ is the direct correlation function.

This picture of local thermodynamics of an inhomogeneous fluid at equilibrium is completed by the generalized compressibility equation in its general form [Eq. (21) of Ref. [6]] or in the form of Eq. (28) of Ref. [6] for the pressure tensor [7] given by Eq. (3.7) above.

IV. DISCUSSION

We have shown that the "pressures" entering into thermal and mechanical descriptions of inhomogeneous fluids at equilibrium are not quite the same, but are related by a scaling transformation. An important consequence is that although the mechanically defined object $\mathbf{P}[n; \mathbf{r}]$ from Eq. (1.1) is not unique, the total volume integral $\int d\mathbf{r} \text{Tr} \mathbf{P}[n; \mathbf{r}]$ must be. Indeed, for a particular

(but very general) class of pressure tensor definitions (3.7) of Ref. [7] automatically satisfying Eq. (1.1), one can easily derive that

$$\int d\mathbf{r} \text{Tr} \mathbf{P}[n; \mathbf{r}] = - \int d\mathbf{r} n(\mathbf{r}) \mathbf{r} \cdot \nabla_{\mathbf{r}} \mu_{\text{in}}[n; \mathbf{r}], \quad (4.1)$$

which is a purely thermodynamic form.

It may be useful to break the abstraction of the analysis and quote one of the very few instances in which the distinction between local pressure and what is effectively grand potential density can be followed in complete detail. This is the case of a hard core (diameter a) fluid in one dimension. Here the local thermodynamic pressure is of course given by

$$\beta P_{\text{th}}(z) = n(z) / [1 - an(z)]. \quad (4.2)$$

But it is also well known that

$$-\beta \Omega = \int_{-\infty}^{\infty} \frac{1}{2} [n(z + \frac{1}{2}a) + n(z - \frac{1}{2}a)] / \left[1 - \int_{z-(1/2)a}^{z+(1/2)a} n(w) dw \right] dz. \quad (4.3)$$

Expanding about $n(z)$, and integrating by parts to reduce to lowest derivatives, the grand potential density can be written as

$$-\beta \omega(z) = n(z) / [1 - an(z)] - (a^3/12) n'(z)^2 [2 - an(z)] / [1 - an(z)]^3 + \dots; \quad (4.4)$$

a difference involving the familiar gradient-square terms. On the other hand, $P(z)$, now determined uniquely [7] by (3.7), for this system, becomes

$$\beta P(z) = n(z) + \int_{z-(1/2)a}^{z+(1/2)a} n(x + \frac{1}{2}a) n(x - \frac{1}{2}a) / \left[1 - \int_{z-(1/2)a}^{z+(1/2)a} n(w) dw \right] dx. \quad (4.5)$$

Integrating over all z and selecting lowest order derivatives, as before, this yields (subscript pt indicates pressure tensor derived)

$$-\beta \omega_{\text{pt}}(z) = n(z) / [1 - an(z)] - (a^3/12) n'(z)^2 \{ 6 - 8an(z) + 3a^2 n(z)^2 / [1 - an(z)] \}^3 + \dots, \quad (4.6)$$

again differing from (4.2) by gradient-square terms:

$$\beta\omega_{pt} - \beta\omega = (a^3/12)n'(z)^2[4 - 3an(z)]/[1 - an(z)]^2 + \dots \quad (4.7)$$

In other words, the mechanical and thermodynamic grand potential densities share, in this difference, the same sort of correction terms that permeate the study of nonuniform fluids.

The analysis developed above for inhomogeneous fluids at equilibrium can be generalized to nonuniform temperature and hence nonequilibrium states of the fluids. This is perfectly feasible, requires only the introduction of an

associated conjugate energy density, and will be reported in a future communication.

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[1] R. Evans, *Adv. Phys.* **28**, 143 (1979).

[2] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982).

[3] H. T. Davis, *J. Chem. Phys.* **86**, 1474 (1987).

[4] L. A. Pozhar and K. E. Gubbins, *J. Chem. Phys.* **94**, 1367 (1991).

[5] L. A. Pozhar and K. E. Gubbins, *J. Chem. Phys.* **99**, 8970 (1993).

[6] L. A. Pozhar, K. E. Gubbins, and J. K. Percus, *Phys. Rev. E* **48**, 1819 (1993).

[7] J. K. Percus, *Chem. Phys. Lett.* **123**, 311 (1986).