*Journal of Statistical Physics, Vol. 100, Nos. 1/2, 2000*

# The Explicit Density Functional and Its Connection with Entropy Maximization

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*Received March 8, 1999; final September 21, 1999*

The intrinsic Helmholtz free energy, commonly used as a basis for density functional theories, is here given explicitly as a cluster diagram expansion with density field points. Also given are explicit variational procedures for determining the chemical potential for a given density, the pair potential for a given pair correlation function, and the pair correlation function for a given pair potential. The physical meaning of the density functional is established within the context of a new derivation of statistical mechanics based on entropy that supplies a variational principle for equilibrium by generalizing the thermodynamic potential to nonequlibrium states. This shows that the conventional density functional determines not only the equilibrium density, but also the probability of fluctuations about that density.

**KEY WORDS:** Density functional theory; cluster diagrams; maximum entropy.

## INTRODUCTION

Although this is a paper about density functional theory, the techniques that it uses are those of functional differentiation and diagrammatic expansion. The classic review of these methods and their application to statistical mechanics remains that of Stell.(1) The art of cluster diagrams is as picturesque as it is powerful, and the key theorems drawn from statistical mechanics are graphically illustrated by this approach. It is not, of course, the strict expansion in powers of density that is really of interest, (although the virial expansion has played a rôle in the theory of gases), but rather the resummation of infinite classes of diagrams that yield tractable equations for dense liquids (e.g., the hypernetted chain equation). Again, this technique of topological reduction has been masterfully sketched by Stell.(1)

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0022-4715/00/0700-0445$18.00/0

Density functional theory is an approach to inhomogeneous fluids that is based upon minimising some free energy or thermodynamic potential. Because of its variational nature, density functional theory has a number of numerical advantages, such as insensitivity to errors in the profile. In addition, robust and universal approximations have been developed for the free energy functional that is to be minimised, and this has resulted in widespread applications of the method.

Obviously for density functional theory to be useable one needs a free energy that is explicitly a functional of the density, which is certainly the case for the approximations just mentioned. Hence the reader may be a little puzzled by the first part of the title of this article. However the concern here is with the formally exact free energy functional that is the basis of the method, not with the various approximate implementations of it. In part the motivation is that such a formally exact functional may provide a source of alternative approximate approaches. In addition, there are conceptual and pedagogic reasons for seeking such an explicit functional.

The free energy density functional that lies at the heart of the theory is typically written(2, 3)

$$\mathscr{F}[\rho] = \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int d\mathbf{p}^N \int d\mathbf{r}^N \{K + U + k_B T \ln \wp\} \, \wp \tag{1}$$

where $\rho(\mathbf{r})$ is the density profile, $K$ is the kinetic energy, and $U$ is the "internal" potential energy, (i.e., that due to the interactions between the particles). The probability of the configuration is the usual Boltzmann factor, $\wp \equiv \exp[-(K + U + V - \mu N)/k_B T]/\Xi$, where $V = \sum_{i=1}^{N} V(\mathbf{r}_i)$ is the external potential, $\mu$ is the chemical potential, and $\Xi$ is the grand partition function, which normalises the probability distribution.

The problem with this is that the right hand side is not an explicit function of density. At equilibrium of course the chemical and external potential appearing in $\wp$ determine the density profile. In so far as there is a one-to-one relationship between the two, which there is, the converse also holds: the density profile determines the configuration probability distribution, $\wp[\rho]$.(4) Hence it is certainly true that the right hand side is an implicit function of the density profile, but it is difficult to see even conceptually how one might actually calculate $\mathscr{F}[\rho]$. The primary point of this paper is to obtain explicitly this density functional.

It turns out that the equilibrium part of the explicit density functional obtained here is equivalent to an expression for the grand potential in terms of density field points given in the aforementioned review by Stell.(1) Over the years the relationship between this equilibrium thermodynamic potential and the non-equilibrium density functional has been obscured, and the pedagogic review that comprises the bulk of Sections 1–3 of this paper may be regarded as a sincere and flattering homage to Stell. Section 4 gives physical meaning to density functional theory using a new derivation of statistical mechanics that is based upon physical entropy maximisation.(5) A careful distinction between equilibrium and non-equilibrium quantities reveals that the explicit density functional is in fact a physical quantity (in essence the constrained total entropy) that determines the non-equilibrium fluctuations in density of the system.

## 1. DIAGRAMMATIC EXPANSIONS

### 1.1. The Grand Potential

Consider a single component fluid whose particles interact with a pairwise additive potential $u(r_{ij})$. In addition there is an external one body potential $V(\mathbf{r})$ that causes a density inhomogeneity $\rho(\mathbf{r})$. The kinetic energy is taken to be the usual quadratic form, and integration over the momenta of the resultant Gaussian yields a factor of the de Broglie thermal wavelength $\Lambda$ for each component. Consequently the grand partition function is(2)

$$\Xi = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{\Lambda^{3N} N!} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp -\beta \left[ \sum_{i=1}^{N} V(\mathbf{r}_i) + \sum_{i<j}^{N} u(r_{ij}) \right] \tag{2}$$

Here and throughout, $\beta \equiv 1/k_B T$, $k_B$ being Boltzmann's constant and $T$ the temperature. This classical Hamiltonian assumes that the potential is pairwise additive and independent of the state of the system, which amongst other things implies that transitions between these states are adiabatic. Defining the generalised activity as

$$z(\mathbf{r}) = \Lambda^{-3} \exp\{[\mu - V(\mathbf{r})]/k_B T\} \tag{3}$$

and the Mayer-$f$ function as $f(r) = -1 + \exp -u(r)/k_B T$, this may be rewritten in a form suitable for diagrammatic expansion,

$$\Xi = \sum_{N=0}^{\infty} \int \frac{d\mathbf{r}^N}{N!} \prod_{i=1}^{N} [z(\mathbf{r}_i)] \prod_{i<j}^{N} [1 + f(r_{ij})] \tag{4}$$

Expanding the Mayer product in powers of activity and $f$-bonds, one has(1, 2)

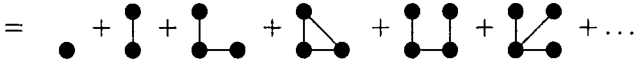
$\Xi = \{$the sum of all distinct simple diagrams with $z$-field points and $f$-bonds$\}$

(5)

A simple diagram is one with at most one bond between any pair of points.

Now the fact that disconnected diagrams appear in this sum indicates that it is the exponential of connected diagrams.(1, 2) Hence the grand potential, which is $\Omega = -k_B T \ln \Xi$, may be expressed as

$\ln \Xi = \{$the sum of all simple connected diagrams with $z$-field points and $f$-bonds$\}$



(6)

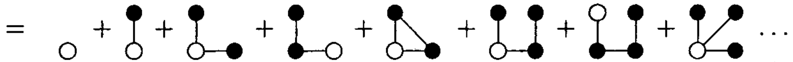
For a homogeneous system, $p = -\Omega/V = k_B T V^{-1} \ln \Xi$, and this provides the expansion of the pressure in powers of the activity.

## 1.2. The Density

The relation between activity and density follows by observing that the ensemble average that is the singlet density may be written as a functional derivative

$$\rho(\mathbf{r}) = z(\mathbf{r}) \frac{\delta \ln \Xi}{\delta z(\mathbf{r})}$$

$= \{$the sum of all simple connected diagrams with a $z$-root point labelled $\mathbf{r}$, and zero or more $z$-field points, and $f$-bonds$\}$



(7)

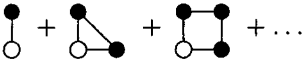
These diagrams may be divided into two sets: those in which the root point is an articulation circle, and those in which it isn't. (An articulation circle is the sole connection between a set of field points and the rest of the diagram.(1, 2)) Taking out the common factor of $z(\mathbf{r})$, the exponential of the so-called star-irreducible diagrams, (those in which the root point is not an articulation circle), yields the diagrams of the entire set.(1, 2) Hence,

$$\ln\frac{\rho(\mathbf{r})}{z(\mathbf{r})} = \{\text{the sum of all simple connected diagrams with a 1-root point labelled } \mathbf{r} \text{ that is not an articulation point, and one or more } z\text{-field points, and } f\text{-bonds}\}$$

$=$  (8)

Now a subset of these diagrams have no articulation points at all; the remainder, in which some field points are articulation points, are just the former with the field points decorated with all the simple connected diagrams with one root point. (Decorate means to attach by the root point at that field point.) But these decorations are just the diagrams of the singlet density, and the procedure corresponds to replacing the $z$-circles by $\rho$-circles. One has

$$\ln\frac{\rho(\mathbf{r})}{z(\mathbf{r})} = \{\text{the sum of all simple irreducible diagrams with a 1-root point labelled } \mathbf{r}, \text{ one or more } \rho\text{-field points, and } f\text{-bonds}\}.$$

$=$  (9)

Here irreducible means free of articulation circles. This is an example of the very powerful procedure of *topological reduction*,$^{(1)}$ whereby an infinite class of diagrams is reduced to a smaller number, (albeit still infinite), of diagrams with simpler structure, by replacing the function attached to each circle or line.

This expression enables the activity of a homogeneous fluid to be given as an expansion in powers of density. Hence the virial expansion of the equation of state, which is the expansion of the pressure in powers of density, can be derived. For a homogeneous fluid, the last expansion may be written

$$\ln z = \ln \rho - \sum_{n=1}^{\infty} \beta_n \rho^n \tag{10}$$

where the $\beta_n$ are the *irreducible Mayer cluster integrals*, as defined above but with unit weight for all circles. Now since $PV/k_B T = \ln \Xi$, then Eq. (7) shows that $(dP/dz) = \rho k_B T/z$, or $(dP/d\rho) = (\rho k_B T/z)(dz/d\rho)$. Hence

$$P = k_B T \int_0^\rho \rho' \frac{d \ln z}{d\rho'} \, d\rho'$$

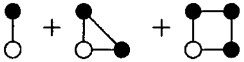
$$= \rho k_B T \left[ 1 - \sum_{n=1}^{\infty} \frac{n}{n+1} \beta_n \rho^n \right] \tag{11}$$

This is the virial expansion, with the virial coefficients being $B_{n+1} = -\beta_n n/(n+1)$.

## 1.3. The Direct and Total Correlation Functions

Equation (7) gives the density as a functional of the activity, $\rho(\mathbf{r}; [z])$, whereas Eq. (9) allows the activity to be written as a functional of the density, $z(\mathbf{r}; [\rho]) = \rho(\mathbf{r}) \exp -c(\mathbf{r})$, where the one particle direct correlation function is

$$c(\mathbf{r}) = \{\text{the sum of all simple irreducible diagrams with a 1-root point labeled } \mathbf{r}\text{, with one or more } \rho\text{-field points, and with } f\text{-bonds}\}$$

$=$  $+ \ldots$ (12)

The reason for wanting to have the density as the independent function rather than the activity (or external field) is that it enables certain variational procedures to be developed. To see this one first notes that the total correlation function is given by$^{(1, 2)}$

$$\frac{z(\mathbf{s}) \, \delta\rho(\mathbf{r})}{\delta z(\mathbf{s})} = \rho(\mathbf{r}) \, \delta(\mathbf{r}, \mathbf{s}) + \rho(\mathbf{r}) \, \rho(\mathbf{s}) \, h(\mathbf{r}, \mathbf{s}) \tag{13}$$

This may also be written as the logarithmic derivative, $\delta\rho(\mathbf{r})/\delta \ln \Lambda^3 z(\mathbf{s})$, where $\ln \Lambda^3 z(\mathbf{s}) = \mu(\mathbf{s})/k_B T = [\mu - V(\mathbf{s})]/k_B T$. Its inverse gives the two particle direct correlation function,

$$\frac{\delta z(\mathbf{r})}{z(\mathbf{r}) \, \delta\rho(\mathbf{s})} = \frac{\delta(\mathbf{r}, \mathbf{s})}{\rho(\mathbf{r})} - c(\mathbf{r}, \mathbf{s}) \tag{14}$$

The combination of these two functional inverses represents the Ornstein–Zernike equation,

$$\int d\mathbf{s} \, \frac{\delta\rho(\mathbf{r})}{\delta z(\mathbf{s})} \frac{\delta z(\mathbf{s})}{\delta\rho(\mathbf{t})} = \delta(\mathbf{r} - \mathbf{t}) \tag{15}$$

or

$$h(\mathbf{r}, \mathbf{t}) = c(\mathbf{r}, \mathbf{t}) + \int d\mathbf{s}\, \rho(\mathbf{s})\, c(\mathbf{r}, \mathbf{s})\, h(\mathbf{s}, \mathbf{t}) \tag{16}$$

Since $z(\mathbf{r}) = \rho(\mathbf{r}) \exp -c(\mathbf{r})$, Eq. (14) may be written

$$\frac{\delta c(\mathbf{r})}{\delta \rho(\mathbf{s})} = c(\mathbf{r}, \mathbf{s}) \tag{17}$$

Continuing in this fashion one builds a hierarchy of direct correlation functions.

## 2. DENSITY FUNCTIONAL THEORY

### 2.1. The Meta-System

Density functional theory consists of varying the density until the minimum of some functional is reached, at which point the functional equals the free energy or thermodynamic potential of the system. At this stage it is purely a mathematical procedure that has no physical basis. Conceptually one may imagine the actual system, with activity $z(\mathbf{r})$, pair potential $e(\mathbf{r}, \mathbf{s}) = \exp -\beta u(\mathbf{r}, \mathbf{s})$, and density $\rho(\mathbf{r})$, and a meta-system with activity $\tilde{z}(\mathbf{r})$, pair potential $\tilde{e}(\mathbf{r}, \mathbf{s})$, and density $\tilde{\rho}(\mathbf{r})$. The configuration probability of the actual system is given by

$$\wp(\mathbf{r}^N) = \frac{1}{\Lambda^{3N} \Xi} \prod_{i=1}^{N} z(\mathbf{r}_i) \prod_{i<j}^{N} e(\mathbf{r}_i, \mathbf{r}_j) \tag{18}$$

Note that the momentum contributions have been incorporated into the thermal de Broglie wavelength $\Lambda$. This probability is normalised so that the grand partition function is

$$\Xi = \sum_{N=0}^{\infty} \int \frac{d\mathbf{r}^N}{\Lambda^{3N} N!} \prod_{i=1}^{N} z(\mathbf{r}_i) \prod_{i<j}^{N} e(\mathbf{r}_i, \mathbf{r}_j) \tag{19}$$

and the grand potential is of course $\Omega = -k_B T \ln \Xi$. Analogous quantities are defined for the meta-system.

In general the derivation of the various functions to be minimised proceeds by adding to the free energy of the actual or of the meta-system a functional that is guaranteed to be positive and to vanish when the two systems coincide. An example of such a functional is the so-called cross-entropy,

$$S[\tilde{\wp}, \wp] = \sum_{N=0}^{\infty} \frac{1}{N!} \int d\mathbf{r}^N\, \tilde{\wp}(\mathbf{r}^N) \ln \frac{\tilde{\wp}(\mathbf{r}^N)}{\wp(\mathbf{r}^N)} \tag{20}$$

In view of the normalisation of the configuration probabilities this may be written

$$S[\tilde{\wp}, \wp] = \sum_{N=0}^{\infty} \int \frac{d\mathbf{r}^N}{N!} \wp(\mathbf{r}^N) \left\{ \frac{\tilde{\wp}(\mathbf{r}^N)}{\wp(\mathbf{r}^N)} \ln \frac{\tilde{\wp}(\mathbf{r}^N)}{\wp(\mathbf{r}^N)} - \frac{\tilde{\wp}(\mathbf{r}^N)}{\wp(\mathbf{r}^N)} + 1 \right\} \tag{21}$$

The integrand is non-negative, (since $x \ln x \geqslant x - 1$), and one concludes that $S[\tilde{\wp}, \wp] \geqslant 0$. Obviously the cross-entropy vanishes if and only if $\tilde{\wp} = \wp$.

There are of course many different functions that have the property of being positive and of vanishing at a desired point, and any of these could be used either in place of, or in addition to the cross-entropy (e.g., $\int d\mathbf{r} [\tilde{\rho}(\mathbf{r}) - \rho(\mathbf{r})]^2$). Hence at this stage the cross-entropy is but one of many mathematical functions that could be used as a basis for a variational procedure for determining the density profile. In Section 4 it will be shown that it is the functionals based upon the cross-entropy itself that have a physical basis, and that minimisation of these functionals in fact corresponds to entropy maximisation.

## 2.2. Variations of the Activity

First one seeks a functional of the activity and the density that is minimised when the activity is the one that would give rise to the specified density. One regards the density as a property of the actual system $\rho(\mathbf{r})$, and the activity that is varied as a property of the meta-system, $\tilde{z}(\mathbf{r})$. The activity of the actual system may be written explicitly as a functional of the density, $z(\mathbf{r}) = \rho(\mathbf{r}) \exp -c(\mathbf{r}; [\rho])$. The pair potential of the meta-system is taken to equal that of the actual system, $\tilde{e}(\mathbf{r}, \mathbf{s}) = e(\mathbf{r}, \mathbf{s})$.

Consider the functional of the meta-activity,

$$\begin{aligned}
\beta\Omega[\tilde{z} \mid \rho] &= -\beta\Omega[z] + \sum_{N=0}^{\infty} \int \frac{d\mathbf{r}^N}{N!} \wp(\mathbf{r}^N) \ln \frac{\wp(\mathbf{r}^N)}{\tilde{\wp}(\mathbf{r}^N)} \\
&= -\beta\Omega[z] + \sum_{N=0}^{\infty} \int \frac{d\mathbf{r}^N}{N!} \wp(\mathbf{r}^N) \ln \frac{\tilde{\Xi}}{\Xi} \prod_{i=1}^{N} \frac{z(\mathbf{r}_i)}{\tilde{z}(\mathbf{r}_i)} \\
&= -\beta\Omega[\tilde{z}] + \int d\mathbf{r}\, \rho(\mathbf{r}) \ln \frac{z(\mathbf{r})}{\tilde{z}(\mathbf{r})} \\
&= -\beta\Omega[\tilde{z}] + \int d\mathbf{r}\, \rho(\mathbf{r}) \left\{ \ln \frac{\rho(\mathbf{r})}{\tilde{z}(\mathbf{r})} - c(\mathbf{r}; [\rho]) \right\}
\end{aligned} \tag{22}$$

It is extremely important to note that in this equation the actual density $\rho$ and the meta-activity $\tilde{z}$ are independent functions, and that they are *not* linked by the equilibrium results established above.

Since the cross-entropy is non-negative, the minimum value of $\Omega[\tilde{z} \mid \rho]$ is $-\Omega[z]$, which is the negative of the grand potential of the actual system. Hence this represents a minimisation procedure for determining the activity that corresponds to a given density. Explicitly, the variation of this functional with respect to activity is

$$\frac{\delta \beta \Omega[\tilde{z} \mid \rho]}{\delta \ln \Lambda^3 \tilde{z}(\mathbf{r})} = \tilde{\rho}(\mathbf{r}) - \rho(\mathbf{r}) \tag{23}$$

The first density that appears on the right hand‘ side is the density of the meta-system determined by the specified activity, whereas the second density is the density of the actual system. This again shows that this functional is minimised with respect to the activity (external field) when the activity is the one that would cause the equilibrium density of the meta-system to equal the specified density, $\rho[\tilde{z}] = \rho$. In other words one now has the basis for a variational procedure for determining $z[\rho]$, or equivalently, for finding the external potential that would give a specified density profile. Perhaps of greatest interest is the application to a homogeneous fluid, where extremisation of the functional gives the chemical potential corresponding to the specified uniform density.

## 2.3. Variations of the Density

The converse procedure is also valuable, and more common. The activity of the actual system, $z$, is now specified as is the density of the meta-system, $\tilde{\rho}$, and one seeks a functional of these two that is minimised when $\tilde{\rho} = \rho[z]$. Again the pair potentials of both systems are identical, and the appropriate functional is

$$\begin{aligned}
\beta \mathscr{F}[\tilde{\rho} \mid z] &= \beta \Omega[z] + \sum_{N=0}^{\infty} \int \frac{d\mathbf{r}^N}{N!} \tilde{\wp}(\mathbf{r}^N) \ln \frac{\tilde{\wp}(\mathbf{r}^N)}{\wp(\mathbf{r}^N)} \\
&= \beta \Omega[z] + \sum_{N=0}^{\infty} \int \frac{d\mathbf{r}^N}{N!} \tilde{\wp}(\mathbf{r}^N) \ln \frac{\Xi}{\tilde{\Xi}} \prod_{i=1}^{N} \frac{\tilde{z}(\mathbf{r}_i)}{z(\mathbf{r}_i)} \\
&= \beta \Omega[\tilde{z}] + \int d\mathbf{r}\, \tilde{\rho}(\mathbf{r}) \ln \frac{\tilde{z}(\mathbf{r})}{z(\mathbf{r})}
\end{aligned} \tag{24}$$

Clearly the minimum value of this functional, which is the grand potential of the actual system, occurs when the density of the meta-system equals that of the actual system. It remains to make this an explicit functional of the meta-density.

Consider $\Omega[\tilde{z}]$, which is the grand potential of the meta-system, and which is implicitly a functional of the density $\tilde{\rho}$. Equation (6) gives the grand potential as a functional of the activity, $\Omega[z]$, and Eq. (9) gives the activity as a functional of the density, $z[\rho]$. Hence the grand potential may be considered to be a functional of the density $\Omega_\rho[\rho] = \Omega[z[\rho]]$, and one has for its derivative

$$\begin{aligned}\frac{-\delta\beta\Omega_\rho[\rho]}{\delta\rho(\mathbf{r})} &= \int \frac{-\delta\beta\Omega[z]}{\delta z(\mathbf{s})}\frac{\delta z(\mathbf{s})}{\delta\rho(\mathbf{r})}\, d\mathbf{s} \\ &= \int \frac{\rho(\mathbf{s})}{z(\mathbf{s})}\frac{\delta z(\mathbf{s})}{\delta\rho(\mathbf{r})}\, d\mathbf{s} \\ &= \int [\delta(\mathbf{r}, \mathbf{s}) - \rho(\mathbf{s})\, c(\mathbf{r}, \mathbf{s})]\, d\mathbf{s} \qquad (25)\end{aligned}$$

The function $\Omega_\rho[\rho]$ is well-defined, at least implicitly. An explicit diagrammatic definition in terms of cluster integrals with density field points will be given shortly.

Now define the thermodynamic potential

$$\mathscr{F}[\rho] = \Omega_\rho[\rho] + k_B T \int d\mathbf{s}\, \rho(\mathbf{s}) \ln \Lambda^3 z(\mathbf{s}; [\rho]) \qquad (26)$$

where $z(\mathbf{s}; [\rho]) = \rho(\mathbf{s}) \exp -c(\mathbf{s}; [\rho])$. This is similar to the Helmholtz free energy, $F = \Omega + \mu N$, except that the external energy is also subtracted; for this reason $\mathscr{F}$ is often referred to as the intrinsic Helmholtz free energy.

Explicitly as a function of density this is

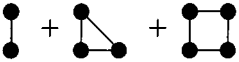
$$\begin{aligned}\beta\mathscr{F}[\rho] = &\int d\mathbf{s}\, \rho(\mathbf{s})[-1 + \ln \Lambda^3 \rho(\mathbf{s})] \\ &- \{\text{the sum of all simple irreducible diagrams with } \rho\text{-field points} \\ &\text{and one or more } f\text{-bonds}\} \qquad (27)\end{aligned}$$

This expression may be split into two parts, $\mathscr{F} = \mathscr{F}^{\text{id}} - \mathscr{F}^{\text{ex}}$, where the ideal part is

$$\beta\mathscr{F}^{\text{id}}[\rho] = \int d\mathbf{s}\, \rho(\mathbf{s})[-1 + \ln \Lambda^3 \rho(\mathbf{s})] \qquad (28)$$

and the excess is

$$\beta\mathcal{F}^{\text{ex}}[\rho] =$$



$$+\cdots \tag{29}$$

The equality of these two expressions for $\mathcal{F}[\rho]$ may be proven by taking the density derivative. Equation (26) yields, using Eqs. (25) and (14),

$$\begin{aligned}\frac{\delta\beta\mathcal{F}[\rho]}{\delta\rho(\mathbf{r})} &= \ln \Lambda^3\rho(\mathbf{r}) - c(\mathbf{r}) \\ &= \ln \Lambda^3 z(\mathbf{r})\end{aligned} \tag{30}$$

But this result also follows from the direct differentiation of Eq. (27) and the diagrammatic definition of the one particle direct correlation function, Eq. (12). Hence the two expressions are equal up to an arbitrary constant independent of density. In the limit of vanishing density, when $z(\mathbf{r}) = \rho(\mathbf{r})$ and $-\beta\Omega_\rho[\rho] = \bullet$, it is clear that the two expressions for $\mathcal{F}[\rho]$ agree, so that the arbitrary constant is zero. This completes the proof of the equivalence of the definitions (26) and (27).

The equivalence of these two definitions of $\mathcal{F}[\rho]$ means that their combination gives an explicit formula for $\Omega_\rho[\rho]$. One has

$$\Omega_\rho[\rho] = k_B T \int d\mathbf{s}\, \rho(\mathbf{s}) \left[ -1 + \ln \frac{\rho(\mathbf{s})}{z(\mathbf{s}; [\rho])} \right] - \mathcal{F}^{\text{ex}}[\rho] \tag{31}$$

where $z(\mathbf{s}; [\rho]) = \rho(\mathbf{s}) \exp -c(\mathbf{s}; [\rho])$. This result is equivalent to Eqs. (7.4) and (7.5) of Ref. 1; the quantity $H[\rho, f]$ of Stell is the present $\mathcal{F}[\rho]$, and his $h_1(\mathbf{r})$ is the present $c(\mathbf{r})$. Stell mentions that this expression for the grand potential in terms of density has been derived by different authors in various fashions.(6–8)

Whereas $\Omega[z]$ acts as a generating functional for the densities, $\mathcal{F}^{\text{ex}}[\rho]$ generates the hierarchy of direct correlation functions upon successive density differentiation. (The full functional $\mathcal{F}[\rho]$ generates terms in addition to the direct correlation function, as in the first member of the hierarchy, Eq. (30).) The second derivative yields the pair direct correlation function,

$$\frac{\delta^2\beta\mathcal{F}[\rho]}{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{s})} = \frac{\delta(\mathbf{r}, \mathbf{s})}{\rho(\mathbf{r})} - c(\mathbf{r}, \mathbf{s}) \tag{32}$$

which is equivalent to the expression given above.

Substitution of this result for $\Omega_\rho[\rho]$ into Eq. (24) yields the explicit density functional,

$$\mathcal{F}[\tilde{\rho} \mid z] = k_B T \int d\mathbf{r}\, \tilde{\rho}(\mathbf{r}) \left[ -1 + \ln \frac{\tilde{\rho}(\mathbf{r})}{z(\mathbf{r})} \right] - \mathcal{F}^{\text{ex}}[\tilde{\rho}] \tag{33}$$

Once again it is emphasised that the density and activity are independent functions here and they are not linked by the equilibrium results established above. Upon differentiation with respect to density one obtains

$$\frac{\delta\beta\mathscr{F}[\tilde{\rho}\,|\,z]}{\delta\tilde{\rho}(\mathbf{r})} = \ln \Lambda^3 z(\mathbf{r};[\tilde{\rho}]) - \ln \Lambda^3 z(\mathbf{r}) \tag{34}$$

Clearly this thermodynamic potential is optimised by the density $\tilde{\rho}(\mathbf{r}) = \rho(\mathbf{r};[z])$, the equilibrium density profile due to the external field $z(\mathbf{r})$. The utility of this variational procedure lies in the availability of tractable approximations for $\mathscr{F}[\rho]$ as a functional of density.

## 3. PAIR DENSITY FUNCTIONAL THEORY

### 3.1. Variation of the Pair Boltzmann Factor

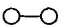
In the above a thermodynamic potential was given in which the activity, $z(\mathbf{r})$, which is the "natural" variable of the grand ensemble, was replaced as independent variable by the normally dependent density $\rho(\mathbf{r})$. In the new ensemble the rôle of external potential and density were interchanged. It is similarly possible to eliminate the pair potential in favor of the pair density.

The total correlation function was given above as essentially the logarithmic activity derivative of the density. It may also be written as the derivative of the grand potential with respect to the pair potential. With $e(\mathbf{r},\mathbf{s}) = \exp -\beta u(\mathbf{r},\mathbf{s})$, one has$^{(1,2)}$

$$\begin{aligned}\frac{\delta\beta\Omega}{\delta \ln e(\mathbf{r},\mathbf{s})} &= \frac{-1}{2}\rho(\mathbf{r},\mathbf{s})\\ &= \frac{-1}{2}\rho(\mathbf{r})\,\rho(\mathbf{s})[1+h(\mathbf{r},\mathbf{s})]\end{aligned} \tag{35}$$

which is to say that

$h(\mathbf{r},\mathbf{s}) = \{$the sum of all simple connected diagrams with two 1-root points labeled $\mathbf{r}$ and $\mathbf{s}$, $\rho$-field points, $f$-bonds, and no articulation points$\}$

=  +  +  + ⋯ (36)

One now seeks to describe a system specified by activity $z$ and pair potential $e = \exp -\beta u$, and with density $\rho$ and total correlation function $h$. One considers a meta-system specified by activity $\tilde{z}$ and pair potential $\tilde{e} = \exp -\beta\tilde{u}$, and with density $\tilde{\rho}$ and total correlation function $\tilde{h}$, and one seeks a functional of the meta-potential that is minimised when $\tilde{h} = h$. Again one invokes the cross-entropy to define the functional

$$\begin{aligned}\beta\Omega[\tilde{e}, \tilde{z} \mid h, \rho] &= -\beta\Omega[e, z] + \sum_{N=0}^{\infty} \int \frac{d\mathbf{r}^N}{N!}\, \wp(\mathbf{r}^N) \ln \frac{\wp(\mathbf{r}^N)}{\tilde{\wp}(\mathbf{r}^N)} \\ &= -\beta\Omega[\tilde{e}, \tilde{z}] + \int d\mathbf{r}\, \rho(\mathbf{r}) \ln \frac{z(\mathbf{r})}{\tilde{z}(\mathbf{r})} \\ &\quad + \frac{1}{2} \int d\mathbf{r}\, d\mathbf{s}\, \rho(\mathbf{r})\, \rho(\mathbf{s}) [1 + h(\mathbf{r}, \mathbf{s})] \ln \frac{e(\mathbf{r}, \mathbf{s})}{\tilde{e}(\mathbf{r}, \mathbf{s})} \end{aligned} \tag{37}$$

Here $z(\mathbf{r}) = z(\mathbf{r}; [h, \rho])$ and $e(\mathbf{r}, \mathbf{s}) = e(\mathbf{r}, \mathbf{s}; [h, \rho])$; the explicit closure formula for $e$ in terms of $h$ will be given in the next section. As far as minimising the functional goes, these two terms are constant, and hence the non-trivial part of the above formula is an explicit function of the pair potential and the activity of the meta-system.

Clearly this functional may be minimised with respect to independent variations of $\tilde{e}$ and of $\tilde{z}$, and its minimum value is the negative of the grand potential of the system. Its respective derivatives are

$$\frac{\delta\beta\Omega[\tilde{e}, \tilde{z} \mid h, \rho]}{\delta \ln \Lambda^3 \tilde{z}(\mathbf{r})} = \tilde{\rho}(\mathbf{r}) - \rho(\mathbf{r}) \tag{38}$$

and

$$\frac{\delta\beta\Omega[\tilde{e}, \tilde{z} \mid h, \rho]}{\delta \ln \tilde{e}(\mathbf{r}, \mathbf{s})} = \frac{\rho(\mathbf{r})\, \rho(\mathbf{s})}{2} [\tilde{h}(\mathbf{r}, \mathbf{s}) - h(\mathbf{r}, \mathbf{s})] \tag{39}$$

Obviously this functional is minimised by the pair potential that would give a total correlation function equal to the specified one. One could imagine that such a variational procedure may be useful in scattering experiments, for example, where the object is to deduce the interaction potential from the measured structure factor.

## 3.2. Variation of the Total Correlation Function

**3.2.1. The Implicit Functional.** Given a system with the pair potential $e(\mathbf{r}, \mathbf{s}) = e^{-\beta u(\mathbf{r}, \mathbf{s})}$, and activity $z(\mathbf{r}) = \Lambda^{-3} \exp \beta[\mu - V(\mathbf{r})])$, the density $\rho(\mathbf{r})$, and the total correlation function $h(\mathbf{r}, \mathbf{s})$ are determined. Here is sought a functional of an arbitrary total correlation function $\widetilde{h}(\mathbf{r}, \mathbf{s})$ that is minimised by the actual total correlation function of the system. In the first instance a meta-system, will be considered, with pair potential $\tilde{e}$, activity $\tilde{z}$, density $\tilde{\rho}$, and total correlation function $\widetilde{h}$.

The functional of the meta-system that is minimised when it coincides with the actual system is

$$\begin{aligned}\Omega[\tilde{e}, \tilde{z} \,|\, e, z] &= \Omega[e, z] + \sum_{N=0}^{\infty} \frac{k_B T}{N!} \int d\mathbf{r}^N \, \tilde{\wp}(\mathbf{r}^N) \ln \frac{\tilde{\wp}(\mathbf{r}^N)}{\wp(\mathbf{r}^N)} \\ &= \Omega[e, z] + \sum_{N=0}^{\infty} \frac{k_B T}{N!} \int d\mathbf{r}^N \, \tilde{\wp}(\mathbf{r}^N) \ln \prod_{i=1}^{N} \frac{\tilde{z}(\mathbf{r}_i)}{z(\mathbf{r}_i)} \prod_{i<j}^{N} \frac{\tilde{e}(\mathbf{r}_i, \mathbf{r}_j)}{e(\mathbf{r}_i, \mathbf{r}_j)} \frac{\Xi}{\tilde{\Xi}} \\ &= \Omega[\tilde{e}, \tilde{z}] + k_B T \int d\mathbf{r} \, \tilde{\rho}(\mathbf{r}) \ln \frac{\tilde{z}(\mathbf{r})}{z(\mathbf{r})} + \frac{k_B T}{2} \int d\mathbf{r} \, d\mathbf{s} \, \tilde{\rho}(\mathbf{r}, \mathbf{s}) \ln \frac{\tilde{e}(\mathbf{r}, \mathbf{s})}{e(\mathbf{r}, \mathbf{s})}\end{aligned} \tag{40}$$

The minimum value of this functional is $\Omega[e, z]$, which is clearly attained when $\tilde{e}(\mathbf{r}, \mathbf{s}) = e(\mathbf{r}, \mathbf{s})$, and $\tilde{z}(\mathbf{r}) = z(\mathbf{r})$. Note that the pair density is $\tilde{\rho}(\mathbf{r}, \mathbf{s}) = \tilde{\rho}(\mathbf{r}) \, \tilde{\rho}(\mathbf{s})[1 + \widetilde{h}(\mathbf{r}, \mathbf{s})]$.

Henceforth the analysis is particularised to the case of fixed density, $\tilde{\rho}(\mathbf{r}) = \rho(\mathbf{r})$. This means that the activity of the meta-system is now a dependent functional, $\tilde{z}(\mathbf{r}) = z(\mathbf{r}; [\tilde{e}, \rho])$.

The derivative of this functional will be required. In view of the fact that

$$\begin{aligned}\frac{\delta \beta \Omega[\tilde{e}, \tilde{z}]}{\delta \widetilde{h}(\mathbf{r}, \mathbf{s})} &= \int d\mathbf{u} \, d\mathbf{t} \, \frac{\delta \beta \widetilde{\Omega}}{\delta \ln \tilde{e}(\mathbf{u}, \mathbf{t})} \frac{\delta \ln \tilde{e}(\mathbf{u}, \mathbf{t})}{\delta \widetilde{h}(\mathbf{r}, \mathbf{s})} + \int d\mathbf{t} \, \frac{\delta \beta \widetilde{\Omega}}{\delta \ln \tilde{z}(\mathbf{t})} \frac{\delta \ln \tilde{z}(\mathbf{t})}{\delta \widetilde{h}(\mathbf{r}, \mathbf{s})} \\ &= \frac{-1}{2} \int d\mathbf{u} \, d\mathbf{t} \, \tilde{\rho}(\mathbf{u}, \mathbf{t}) \frac{\delta \ln \tilde{e}(\mathbf{u}, \mathbf{t})}{\delta \widetilde{h}(\mathbf{r}, \mathbf{s})} - \int d\mathbf{t} \, \tilde{\rho}(\mathbf{t}) \frac{\delta \ln \tilde{z}(\mathbf{t})}{\delta \widetilde{h}(\mathbf{r}, \mathbf{s})}\end{aligned} \tag{41}$$

it follows that for fixed density, $\tilde{\rho}(\mathbf{r}) = \rho(\mathbf{r})$,

$$\frac{\delta \beta \Omega[\tilde{e} \,|\, e, z]}{\delta \widetilde{h}(\mathbf{r}, \mathbf{s})} = \frac{1}{2} \rho(\mathbf{r}) \, \rho(\mathbf{s}) \ln \frac{\tilde{e}(\mathbf{r}, \mathbf{s})}{e(\mathbf{r}, \mathbf{s})} \tag{42}$$

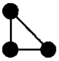
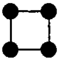
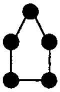
**3.2.2. The Explicit Functional.** This functional may be written as an explicit functional of the the total correlation function. One requires the closure relationship and two generating functions for the classes of diagrams that appear therein.

The diagrams comprising the total correlation function may be divided into several classes. First there is the series function, which is the sum of all diagrams with nodes, where a node is a field point through which all paths connecting the root points pass. The diagrams without nodes comprise the pair direct correlation function $c(\mathbf{r}, \mathbf{s})$ given above, so that the series function may be written $h(\mathbf{r}, \mathbf{s}) - c(\mathbf{r}, \mathbf{s})$. Furthermore, one may identify those diagrams in which the root points do not form an articulation pair of points, (and which do not have an $f(\mathbf{r}, \mathbf{s})$ bond), and it follows that the exponential of these, (times $e(\mathbf{r}, \mathbf{s})$, less 1), generates the total correlation function itself. The exponent comprises the series function, and the remainder, which is called the bridge function, $d(\mathbf{r}, \mathbf{s})$. These observations and definitions allow the total correlation function to be written,$^{(1, 2)}$

$$h(\mathbf{r}, \mathbf{s}) = -1 + e(\mathbf{r}, \mathbf{s})\, e^{h(\mathbf{r}, \mathbf{s}) - c(\mathbf{r}, \mathbf{s}) + d(\mathbf{r}, \mathbf{s})} \tag{43}$$

Now one needs to define two sets of diagrams that will yield the series function $h - c$ and the bridge function $d$ when differentiated with respect to the total correlation function. A ring is a linear chain closed on itself, and one defines the ring diagrams as

$\mathscr{R}[h] = \{$the sum of all simple connected diagrams with $(-\rho)$-field points and $h$-bonds, such that each field point is intersected by exactly two bonds$\}$

$=$ $-$  $+$  $-$  $+\cdots$ (44)

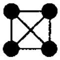
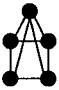
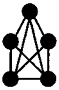
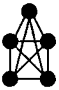
Differentiation yields the series function,

$$\begin{aligned}\frac{\delta \mathscr{R}[h]}{\delta h(\mathbf{r}, \mathbf{s})} &= \frac{1}{2} \rho(\mathbf{r})\, \rho(\mathbf{s}) [-h * h + h * h * h - h * h * h * h + \cdots](\mathbf{r}, \mathbf{s}) \\ &= \frac{-1}{2} \rho(\mathbf{r})\, \rho(\mathbf{s}) [h * c](\mathbf{r}, \mathbf{s}) \\ &= \frac{-1}{2} \rho(\mathbf{r})\, \rho(\mathbf{s}) [h(\mathbf{r}, \mathbf{s}) - c(\mathbf{r}, \mathbf{s})] \end{aligned} \tag{45}$$

Here the Ornstein–Zernike equation has been used; the asterisks denote a density-weighted convolution integral.

The second function is defined as

$\mathcal{B}[h] = \{$the sum of all simple connected diagrams with four or more $\rho$-field points and no articulation points, and with $h$-bonds and no articulation pairs of points$\}$

$=$  $+$  $+$  $+$  $+\cdots$ (46)

Differentiation yields the bridge function,

$$\frac{\delta\mathcal{B}[\rho, h]}{\delta h(\mathbf{r}, \mathbf{s})} = \frac{1}{2}\rho(\mathbf{r})\,\rho(\mathbf{s})\,d(\mathbf{r}, \mathbf{s}) \tag{47}$$

Using these definitions, the explicit functional of the total correlation function is

$$\begin{aligned}\beta\mathcal{G}[\tilde{h} \mid e, z] = {} & \int d\mathbf{r}\,\rho(\mathbf{r})\left[\ln\frac{\rho(\mathbf{r})}{z(\mathbf{r})} - 1\right] + \mathcal{R}[\tilde{h}] - \mathcal{B}[\tilde{h}] \\ & + \frac{1}{2}\int d\mathbf{r}\,d\mathbf{s}\,\rho(\mathbf{r})\,\rho(\mathbf{s})\{[1 + \tilde{h}(\mathbf{r}, \mathbf{s})]\ln[1 + \tilde{h}(\mathbf{r}, \mathbf{s})] - \tilde{h}(\mathbf{r}, \mathbf{s})\} \\ & - \frac{1}{2}\int d\mathbf{r}\,d\mathbf{s}\,\rho(\mathbf{r})\,\rho(\mathbf{s})[1 + \tilde{h}(\mathbf{r}, \mathbf{s})]\ln e(\mathbf{r}, \mathbf{s})\end{aligned} \tag{48}$$

Using the closure, Eq. (43), differentiation yields

$$\frac{\delta\beta\mathcal{G}[\tilde{h} \mid e, z]}{\delta\tilde{h}(\mathbf{r}, \mathbf{s})} = \frac{1}{2}\rho(\mathbf{r})\,\rho(\mathbf{s})\ln\frac{\tilde{e}(\mathbf{r}, \mathbf{s})}{e(\mathbf{r}, \mathbf{s})} \tag{49}$$

which shows that up to a constant independent of $\tilde{h}$ this explicit functional is the same as the implicit one, Eq. (40).

The value of the constant may be determined by taking the high temperature limit, $\tilde{f} \to 0$. It is straightforward to show that

$$\beta\Omega[\tilde{e} \mid e, z] \to \int d\mathbf{r}\,\rho(\mathbf{r})\left[-1 + \ln\frac{\rho(\mathbf{r})}{z(\mathbf{r})}\right] - \frac{1}{2}\int d\mathbf{r}\,d\mathbf{s}\,\rho(\mathbf{r})\,\rho(\mathbf{s})\ln e(\mathbf{r}, \mathbf{s}) \tag{50}$$

But is clear that this is also the high temperature limit of $\mathcal{G}[\tilde{h} \mid e, z]$, so one concludes that the two functionals are in fact identical, $\mathcal{G}[\tilde{h} \mid e, z] = \Omega[\tilde{e} \mid e, z]$, and that $\Omega[e, z] = \mathcal{G}[h \mid e, z]$.

It is obvious that the pair potential determines the pair correlation function. The fact that an explicit functional was given above indicates that the obverse holds; one can also prove this directly in a fashion similar to that employed for the singlet density.$^{(2)}$ In other words, there is a unique pair potential for each pair density, which means that well may one write $e(\mathbf{r}, \mathbf{s}; [h])$.

Stell gives in Eq. (10.13) of ref. 1 an explicit expression for the grand potential as a functional of the singlet and pair density that is equivalent to the present expression for $\mathscr{G}[h \mid e, z]$ (at equilibrium); Stell's $W[\rho, h]$ is the present $\mathscr{B}[h] - \mathscr{R}[h]$. Although Stell is dealing purely with the equilibrium situation, he does state that if his expression is rearranged so that the pair potential (and also the activity) appear explicitly, and if they are regarded as fixed while the total correlation function (and the density) are varied, then the resultant functional is minimised by the equilibrium values. This non-equilibrium functional, (apart from the activity), is the same as the present $\mathscr{G}[\tilde{h} \mid e, z]$.

### 3.2.3. The HNC Approximation.

The ring diagrams are readily evaluated, at least in the uniform density case, $\rho(\mathbf{r}) = \rho$, $h(\mathbf{r}, \mathbf{s}) = h(|\mathbf{r} - \mathbf{s}|)$. One has $\mathscr{R}[h] = \sum_{n=3}^{\infty} \mathscr{R}_n$, with

$$\begin{aligned}
\mathscr{R}_n &= \frac{(-\rho)^n}{2n} \int d\mathbf{r}_1 \cdots d\mathbf{r}_n h(r_{12})\, h(r_{23}) \cdots h(r_{n-1,n})\, h(r_{n,1}) \\
&= \frac{(-\rho)^n V}{2n} \int d\mathbf{r}_{12} h(r_{12})\, H_{n-1}(r_{21}) \\
&= \frac{(-\rho)^n V}{2n(2\pi)^3} \int d\mathbf{k}\, \hat{h}(k)\, \hat{H}_{n-1}(k) \\
&= \frac{(-\rho)^n V}{2n(2\pi)^3} \int d\mathbf{k}\, \hat{h}(k)^n
\end{aligned} \tag{51}$$

where the circumflex denotes the Fourier transform and Parsevaal's theorem and the convolution theorem have been used. It follows that

$$\begin{aligned}
\mathscr{R}[h] &= \frac{V}{2(2\pi)^3} \int d\mathbf{k} \{\ln[1 + \rho\hat{h}(k)] - \rho\hat{h}(k) + \rho^2\hat{h}(k)^2/2\} \\
&= \frac{V}{2(2\pi)^3} \int d\mathbf{k} \{\ln[1 + \rho\hat{h}(k)] - \rho\hat{c}(k)\} - \frac{V\rho^2}{2} \int d\mathbf{r} \left\{ c(r)\, h(r) - \frac{h(r)^2}{2} \right\}
\end{aligned} \tag{52}$$

where the Ornstein–Zernike equation has been used, $\hat{h}(k) = \hat{c}(k) + \rho\hat{c}(k)\, \hat{h}(k)$.

The hypernetted chain (HNC) approximation consists of the neglect of the bridge diagrams $\mathscr{B}[h]=0$. The rationale for this approximation is that in general the bridge diagrams are difficult to compute, although in recent years considerable progress has been made.$^{(9-11)}$ One has

$$\beta\mathscr{G}^{\mathrm{HNC}}[\tilde{h}\mid e, z]/V=\rho\ln\rho-\rho-\rho\beta\mu+\mathscr{R}[\tilde{h}]/V-\frac{\rho^2}{2}\int d\mathbf{r}[1+\tilde{h}(r)]\ln e(r) \\ +\frac{\rho^2}{2}\int d\mathbf{r}\{[1+\tilde{h}(r)]\ln[1+\tilde{h}(r)]-\tilde{h}(r)\} \tag{53}$$

This HNC functional to be minimised is the same as that given by Olivares and McQuarrie.$^{(12)}$ Using the HNC closure, $h(r)=-1+e(r)\exp[h(r)-c(r)]$, this may be rewritten as

$$\beta\mathscr{G}^{\mathrm{HNC}}[\tilde{h}\mid e, z]/V=\rho\ln\rho-\rho-\rho\beta\mu+\mathscr{R}[\tilde{h}]/V+\frac{\rho^2}{2}\int d\mathbf{r}[1+\tilde{h}(r)]\ln\frac{\tilde{e}(r)}{e(r)} \\ +\frac{\rho^2}{2}\int d\mathbf{r}\{\tilde{h}(r)^2-\tilde{h}(r)\,\tilde{c}(r)-\tilde{c}(r)\} \tag{54}$$

from which it is apparent that its minimum value, which is the grand potential, is

$$\frac{\beta\Omega^{\mathrm{HNC}}}{V}=\rho\ln\rho-\rho-\rho\beta\mu+\frac{\rho^2}{2}\in t\; d\mathbf{r}\left\{\frac{h(r)^2}{2}-c(r)\right\} \\ -\int\frac{d\mathbf{k}}{16\pi^3}\{\ln[1+\rho\hat{h}(k)]-\rho\hat{c}(k)\} \tag{55}$$

In so far as the grand potential may be written as a Legendre transform of the Helmholtz free energy, $\Omega=F-N\mu$, one may recognise in this the known result for the HNC excess Helmholtz free energy$^{(13,\,14)}$

$$\beta F_{\mathrm{ex}}^{\mathrm{HNC}}/V=\frac{\rho^2}{2}\int d\mathbf{r}\{h(r)^2/2-c(r)\} \\ -\int\frac{d\mathbf{k}}{16\pi^3}\{\ln[1+\rho\hat{h}(k)]-\rho\hat{c}(k)\} \tag{56}$$

Finally, it is worth mentioning that the HNC expression for the excess chemical potential may also be given explicitly. It is$^{(13-15)}$

$$\beta\mu_{\mathrm{ex}}^{\mathrm{HNC}}=\frac{\rho}{2}\int d\mathbf{r}\{h(r)^2-h(r)\,c(r)-2c(r)\} \tag{57}$$

## 4. THE MEANING OF DENSITY FUNCTIONAL THEORY

The density functional $\mathscr{F}[\tilde{\rho} \mid z]$ is well-defined mathematically by the above results, which show that it is optimised by the equilibrium density. However the physical basis and interpretation of the functional is not in evidence, and it is the purpose of the present section to clarify these. More generally the classic thermodynamic potentials of thermodynamics and statistical mechanics are often said to be minimal at equilibrium, despite the fact that they are traditionally defined only for the equilibrium state. This issue may be clarified by basing the derivation of statistical mechanics, directly on entropy, which enables a non-equilibrium potential to be well-defined.(5) What follows is an abbreviated account of that portion of the derivation relevant to density functional theory. It begins with the fundamental definition of entropy, moves quickly to a uniform open system, and concludes with the singlet density functional derived above.

### 4.1. Entropy

One begins with *microstates*, which are the disjoint, distinct, indivisible states of the system. To each microstate $i$ is attached a non-negative weight $\omega_i$, and the probability that a system is in a particular microstate is proportional to this weight, $\wp_i = \omega_i / W$, where $W = \sum_i \omega_i$ is the total weight of the system. In passing from the discrete to the continuum, one has to introduce a measure for the space of microstates, and the weights and the probability density depend upon this measure, and transform between spaces as the measure itself. Statistical thermodynamics deduces various results postulating the existance of microstates; it is the task of statistical mechanics to identify the microstates and to give their weight. In classical statistical mechanics, it is conventional to take phase space as having uniform measure, either axiomatically or as a consequence of the ergodic hypothesis. In the thermodynamic limit any reasonable non-uniform measure contributes negligibly in comparison with the variation of the exponential terms.(5)

The fundamental axiom or definition of statistical thermodynamics is

the entropy of the system is $k_B$ times the logarithm of the total weight (58)

In the event that the microstates are all equally likely, the total weight may be taken to be the total number of microstates, in which case this is just Boltzmann's definition of the entropy.

*Macrostates* are distinct, disjoint sets of microstates, and the weight of a macrostate $\alpha$ is the sum of the weights of the microstates that it encompasses, $\omega_\alpha = \sum_{i \in \alpha} \omega_i$. By analogy with the above one defines

$$\text{the entropy of a macrostate is } k_B \text{times the logarithm of the total weight of the corresponding microstates} \tag{59}$$

or $S_\alpha = k_B \ln \omega_\alpha$. With this definition the probability of a macrostate is

$$\wp_\alpha = \frac{\omega_\alpha}{W} = Z^{-1} \exp S_\alpha / k_B \tag{60}$$

where the normalising partition function is evidently the total weight of the system $Z = W$. It follows that the entropy of the system is the logarithm of the partition function. Direct substitution shows that the entropy of the system may be written as a functional of the probability distribution,

$$\begin{aligned} S &\equiv k_B \ln Z \\ &= \sum_\alpha \wp_\alpha [S_\alpha - k_B \ln \wp_\alpha] \end{aligned} \tag{61}$$

This is *the* correct expression for $S[\wp]$, and it is entirely equivalent to the above generalisation to non-uniform spaces of Boltzmann's original result. By implication the conventional Gibbs–Shannon formula commonly used in the literature is incorrect, (as is Jaynes' maximum entropy principle, which is based upon it), because it neglects the entropy of the macrostate, (the first term in the brackets).

## 4.2. Uniform Open System

The entropy of an isolated system with energy $E$, number of particles $N$, and volume $V$ is denoted $S(E, N, V)$. The temperature is defined by the energy derivative of this, and the chemical potential is defined by the number derivative,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}, \qquad \frac{-\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V} \tag{62}$$

Now consider this a sub-system able to exchange energy and particles with a reservoir, the total of each being conserved. The microstates of the total system are fundamental in the sense of the primary axiom, and the macrostates of the total system are labeled by the values of energy and number of the sub-system. By definition a reservoir is very much larger than the sub-system, and, in the thermodynamic limit, the subsystem, is very much larger than the region of interaction of the two. It follows that the total entropy for a particular macrostate is the sum of the sub-system entropy and the reservoir entropy, each considered as isolated and constrained to their respective state. A Taylor expansion of the reservoir entropy yields

$$S(\tilde{E}, \tilde{N} \mid \mu, V, T) = S(\tilde{E}, \tilde{N}, V) - \frac{\tilde{E}}{T} + \frac{\mu \tilde{N}}{T} \tag{63}$$

(Here and throughout a constant independent of the presence of the sub-system is neglected.) The left hand side is the constrained total entropy, the first term on the right is the entropy of the sub-system in the particular macrostate, and the remainder is the sub-system dependent part of the reservoir entropy in the macrostate. The quantities with a tilde refer to the sub-system, and the quantities without refer to the reservoir, (except for the sub-system volume $V$).

The equilibrium state is defined as the macrostate with the most weight, (or most number of microstates r if they are equally likely). Equivalently, it is the state of maximum constrained total entropy. The vanishing of the derivative of the above gives this maximal macrostate, so that equilibrium occurs when

$$\frac{\partial S(\tilde{E}, \tilde{N}, V)}{\partial \tilde{E}} = \frac{1}{T}, \qquad \frac{\partial S(\tilde{E}, \tilde{N}, V)}{\partial \tilde{N}} = \frac{-\mu}{T} \tag{64}$$

In words, at equilibrium one has temperature and chemical potential equality between the sub-system and the reservoir, $T(\overline{E}, \overline{N}, V) = T$, and $\mu(\overline{E}, \overline{N}, V) = \mu$. An overline is used to denote the equilibrium state. It may be shown that the entropy must be a concave function in any state that can represent equilibrium with a reservoir, which delimits the stable states of matter, and which proves that the extremum is a maximum.

One defines in general the fluctuation potential to be the negative of the temperature times the constrained total entropy. In this case it is

$$\begin{aligned} \Omega(\tilde{E}, \tilde{N} \mid \mu, V, T) &= -TS(\tilde{E}, \tilde{N} \mid \mu, V, T) \\ &= \tilde{E} - \mu \tilde{N} + S(\tilde{E}, \tilde{N}, V) \end{aligned} \tag{65}$$

It ought be obvious that the fluctuation potential is a non-equilibrium quantity. Since the probability of a macrostate is the exponential of the entropy one has

$$\wp(\tilde{E}, \tilde{N} \mid \mu, V, T) = \frac{e^{-\Omega(\tilde{E}, \tilde{N} \mid \mu, V, T)/k_B T}}{\Xi(\mu, V, T)} \tag{66}$$

The logarithm of the partition function is the total unconstrained entropy, $S_\mu(\mu, V, T) = k_B \ln \Xi(\mu, V, T)$.

Because the entropy is concave, the fluctuation potential, which is its negative, is convex. In general the thermodynamic potential is defined to be the minimum value of the fluctuation potential, which obviously occurs for the equilibrium state. In the present case it is called the grand potential,

$$\begin{aligned}\Omega(\mu, V, T) &= \Omega(\bar{E}, \bar{N} \mid \mu, V, T)\\ &= \bar{E} - \mu\bar{N} - TS(\bar{E}, \bar{N}, V)\end{aligned} \tag{67}$$

Again it is emphasised that the thermodynamic potential is purely an equilibrium quantity; it is the fluctuation potential that is minimised at equilibrium, not the thermodynamic potential. Because it gives directly their probability, the fluctuation potential is *the* extension of the thermodynamic potential to non-equlibrium states.

The variational nature of the fluctuation potential makes differentiation of the thermodynamic potential particularly simple. For example,

$$\begin{aligned}\frac{\partial\Omega(\mu, V, T)}{\partial\mu} &= \frac{\partial\Omega(\bar{E}, \bar{N} \mid \mu, V, T)}{\partial\mu}\\ &= \frac{\partial\bar{E}}{\partial\mu} - \bar{N} - \mu\frac{\partial\bar{N}}{\partial\mu} - T\frac{\partial S(\bar{E}, \bar{N}, V)}{\partial\bar{E}}\frac{\partial\bar{E}}{\partial\mu} - T\frac{\partial S(\bar{E}, \bar{N}, V)}{\partial\bar{N}}\frac{\partial\bar{N}}{\partial\mu}\\ &= -\bar{N}\end{aligned} \tag{68}$$

since in the equilibrium state $\bar{T} = T$ and $\bar{\mu} = \mu$. Effectively then, the equilibrium quantities may be held fixed during differentiations such as these.

In the above it was stated that the logarithm of the partition function gave the unconstrained total entropy, where the partition function is the weighted sum over the macrostates. If fluctuations are negligible, which they are in the thermodynamic limit, this sum is dominated by its largest term, which is of course the equilibrium macrostate. Hence one has

$$\begin{aligned}S_\mu(\mu, V, T) &= k_B \ln \Xi(\mu, V, T)\\ &= k_B \ln \sum_{\tilde{E}, \tilde{N}} e^{S(\tilde{E}, \tilde{N} \mid \mu, V, T)/k_B}\\ &\approx k_B \ln e^{S(\bar{E}, \bar{N} \mid \mu, V, T)/k_B}\\ &= -\Omega(\mu, V, T)/T\end{aligned} \tag{69}$$

which is of course the conventional result, that the thermodynamic potential is in essence the logarithm of the partition function. It is emphasised that this conventional equality only holds in the thermodynamic limit whereas equating the logarithm of the partition function to the total unconstrained entropy holds in general.

In the above three different entropies appeared and one must keep in mind the distinction between them: there is the entropy of an isolated system in a certain state, $S(E, N, V)$, there is the constrained total entropy of a macrostate, $S(\tilde{E}, \tilde{N} \mid \mu, V, T)$, and there is the unconstrained total entropy, $S_\mu(\mu, V, T)$. The last quantity is the logarithm of the total number of microstates of the total system, (apart from a constant independent of the sub-system), whereas $S(\tilde{E}, \tilde{N} \mid \mu, V, T)$ is the sum of the entropy of the sub-system and the reservoir, each considered as isolated and constrained in their respective state.

Conventional derivations derive the thermodynamic potentials as Legendre transforms of the energy, (e.g., [16, Section 5.3]), which by the definition of such transforms restricts them purely to the equilibrium state, and precludes them obeying a variational principle. Callan [16, Section 6.1] does show that for a composite sub-system in contact with a reservoir, the (composite) thermodynamic potential provides a variational principle for an *internal* constraint, provided that *external* equilibrium with the reservoir is maintained. The present fluctuation potential provides a variational principle for the external equilibrium itself. By avoiding the Legendre transform the present derivation establishes the physical connection between the fluctuation potential and the constrained total entropy. In contrast, the fluctuation potential postulated by Callan [16, Postulate II', Section 15.1] is simply regarded as a mathematical function, namely a (generalised) Legendre transform of the entropy. Because of its relationship to the fluctuation potential, the present derivation also supplies a physical interpretation to the thermodynamic potentials, namely as the maximal constrained total entropy, which is approximately equal to the unconstrained total entropy.

### 4.3. The Density Functional

The above procedures may be used to derive all the common systems and ensembles of thermodynamics and statistical mechanics,[(5)] but now the focus is on the interpretation of density functional theory. The expression for the constrained total entropy, Eq. (63), may be rewritten as

$$S(\tilde{E}, \tilde{N} \mid \mu, V, T) = \left[ S(\tilde{E}, \tilde{N}, V) - \frac{\tilde{E}}{\tilde{T}} + \frac{\tilde{\mu}\tilde{N}}{\tilde{T}} \right] - \tilde{E} \left\{ \frac{1}{T} - \frac{1}{\tilde{T}} \right\} + \tilde{N} \left\{ \frac{\mu}{T} - \frac{\tilde{\mu}}{\tilde{T}} \right\} \tag{70}$$

The term in brackets represents the constrained total entropy of the equilibrium macrostate of a sub-system and reservoir with temperature $\tilde{T}$ and chemical potential $\tilde{\mu}$. This reservoir may be called the meta-reservoir, to distinguish it from the actual reservoir $T$, $\mu$, and the constrained total entropy of the meta-system may be denoted $S(\tilde{E}, \tilde{N} \mid \tilde{\mu}, V, \tilde{T})$. As discussed above, when fluctuations are negligible the equilibrium state dominates, and this term may be approximated as the unconstrained total entropy of the sub-system and meta-reservoir, $S_\mu(\tilde{\mu}, V, \tilde{T})$. The two terms in braces represent the difference between the entropies of the actual and of the meta-reservoir, when the sub-system is in the macrostate $\tilde{E}$, $\tilde{N}$. Hence this may be written

$$\begin{aligned} S(\tilde{E}, \tilde{N} \mid \mu, V, T) &= S(\tilde{E}, \tilde{N} \mid \tilde{\mu}, V, \tilde{T}) + \Delta S_{\text{res}}(\tilde{E}, \tilde{N}) \\ &\approx S_\mu(\tilde{\mu}, V, \tilde{T}) + \Delta S_{\text{res}}(\tilde{E}, \tilde{N}) \end{aligned} \tag{71}$$

This particular result may be stated more generally: the constrained total entropy of a sub-system and reservoir may be written as the total entropy of the sub-system and meta-reservoir, plus the entropy of the actual reservoir (for the macrostate), less the entropy of the meta-reservoir (for the macrostate). The meta-resevoir is chosen to yield the given macrostate as the equilibrium state. Parenthetically one may add that since fluctuations are negligible in the thermodynamic limit, the constrained total entropy of the sub-system and meta-reservoir may be approximated as the unconstrained total entropy of the sub-system and meta-reservoir.

In the case that the reservoir imposes an external potential $V(\mathbf{r})$ that causes a density inhomogeneity $\rho(\mathbf{r})$, one divides the energy of the sub-system into an internal and an external part. If the sub-system is in the macrostate $\tilde{\rho}(\mathbf{r})$, then the particle number and the external energy are given by

$$\tilde{N} = \int d\mathbf{r}\, \tilde{\rho}(\mathbf{r}), \qquad \tilde{E}^{\text{ext}} = \int d\mathbf{r}\, \tilde{\rho}(\mathbf{r})\, V(\mathbf{r}) \tag{72}$$

Writing the local chemical potential of the reservoir as $\mu(\mathbf{r}) = \mu - V(\mathbf{r})$, the constrained total entropy of the sub-system and reservoir is

$$\begin{aligned} &S(\tilde{E}, [\tilde{\rho}] \mid [\mu], V, T) \\ &\quad = S(\tilde{E}, [\tilde{\rho}], V) - \frac{\tilde{E}}{T} + \frac{1}{T} \int d\mathbf{r}\, \tilde{\rho}(\mathbf{r})\, \mu(\mathbf{r}) \end{aligned}$$

$$
\begin{aligned}
&= S(\tilde{E}, [\tilde{\rho}], V) - \frac{\tilde{E}}{\tilde{T}} + \frac{1}{\tilde{T}} \int d\mathbf{r}\, \tilde{\rho}(\mathbf{r})\, \tilde{\mu}(\mathbf{r}) \\
&\quad - \tilde{E} \left\{ \frac{1}{T} - \frac{1}{\tilde{T}} \right\} + \int d\mathbf{r}\, \tilde{\rho}(\mathbf{r}) \left\{ \frac{\mu(\mathbf{r})}{T} - \frac{\tilde{\mu}(\mathbf{r})}{\tilde{T}} \right\} \\
&= S(\tilde{E}, [\tilde{\rho}] \,|\, [\tilde{\mu}], V, \tilde{T}) - \tilde{E} \left\{ \frac{1}{T} - \frac{1}{\tilde{T}} \right\} + k_B \int d\mathbf{r}\, \tilde{\rho}(\mathbf{r}) \ln \frac{z(\mathbf{r})}{\tilde{z}(\mathbf{r})} \qquad (73)
\end{aligned}
$$

Here $\tilde{E}$ is the internal energy of the sub-system, and in making the Taylor expansion of the reservoir, use has been made of the fact that for the given macrostate the energy of the reservoir is $E_0 - \tilde{E} - \tilde{E}^{\mathrm{ext}}$. The final equality follows by using the definition of the activity, $z(\mathbf{r}) = \Lambda^{-3} \exp \beta\mu(\mathbf{r})$. In the case that the sub-system is thermally equilibrated, $\tilde{T} = T$, one has

$$
S([\tilde{\rho}] \,|\, [z], V, T) = S([\tilde{\rho}] \,|\, [\tilde{z}], V, T) + k_B \int d\mathbf{r}\, \tilde{\rho}(\mathbf{r}) \ln \frac{z(\mathbf{r})}{\tilde{z}(\mathbf{r})} \qquad (74)
$$

where the activity rather than the chemical potential is now used. (As discussed above, for a macroscopic system one can approximate the constrained total entropy of the equilibrium meta-state by the unconstrained total entropy $S([\tilde{\rho}] \,|\, [\tilde{z}], V, T) \approx S_z([\tilde{z}], V, T)$.) Since in general the fluctuation potential is the negative of the temperature times the constrained entropy, multiplying by $-T$ one may write this as

$$
\mathscr{F}[\tilde{\rho} \,|\, z] = \Omega[\tilde{z}] + k_B T \int d\mathbf{r}\, \tilde{\rho}(\mathbf{r}) \ln \frac{\tilde{z}(\mathbf{r})}{z(\mathbf{r})} \qquad (75)
$$

The grand potential of the meta-system appears as the first term on the right hand side because the given macrostate is the equilibrium state for the sub-system in contact with the meta-reservoir; its fluctuation potential is at its minimum value, $\Omega[\tilde{\rho} \,|\, \tilde{z}] = \Omega[\tilde{z}]$. This expression for $\mathscr{F}[\tilde{\rho} \,|\, z]$ is of course precisely the one obtained for the density functional in the text.

In view of the above derivation of statistical mechanics, a physical meaning can now be given to density functional theory. The density functional $\mathscr{F}[\tilde{\rho} \,|\, z]$ is nothing but the fluctuation potential, which is (the negative of the temperature times) the entropy of the sub-system when it has a particular density profile, plus the entropy of the reservoir in the corresponding macrostate. Minimisation of the density functional corresponds to maximisation of the constrained total entropy, which is the procedure for establishing the equilibrium macrostate. Furthermore, the density functional is unique: whereas there are many functionals that are mathematically minimised at equilibrium, it is the present one that determines the density fluctuations of the ensemble. The above analysis shows that the probability of such fluctuations is given by

$$\wp[\tilde{\rho} \mid z] = \frac{1}{\Xi[z]} e^{-\beta \mathcal{F}[\tilde{\rho} \mid z]} \tag{76}$$

The left hand side may be visualised by sub-dividing space into cells $\mathbf{r}_i$ of size $\Delta_i$, so that for a given density $\tilde{\rho}(\mathbf{r})$ the cell occupancy is $\tilde{n}_i = \Delta_i \tilde{\rho}(\mathbf{r}_i)$, and the entire density function is represented by the set of occupancies $\underline{\tilde{n}}$. The left hand side then (represents the joint probability for the cells to be so occupied. The measure of this probability is conventionally taken as uniform, although there is a Bayesian argument that it should be taken as the Cartesian product of Jeffries' priors, $\propto \prod_i \tilde{n}_i^{-1}$

Obviously, one can make an analogous interpretation of the pair functional $\mathcal{G}[\tilde{h} \mid e]$.

### 4.4. The Activity Functional

In the text a functional of the activity was given, $\Omega[\tilde{z} \mid \rho]$, that was minimised by the activity that would yield the specified density, (i.e., when $\rho(\mathbf{r}; [\tilde{z}]) = \rho(\mathbf{r})$, or equivalently when $\tilde{z}(\mathbf{r}) = z(\mathbf{r}; [\rho])$). For a homogenous system in the absence of an external field this functional is

$$\Omega(\tilde{\mu} \mid N) = -\Omega(\tilde{\mu}) + N(\mu - \tilde{\mu}) \tag{77}$$

where $\mu = \mu(N)$ is the chemical potential corresponding to $N$. Note that here and throughout this section all the functions depend upon the fixed $V$ and $\tilde{T}$ (or $T$), which are not shown explicitly.

This result may be derived from the fluctuation potential for a subsystem exchanging particles and energy with a reservoir,

$$\begin{aligned} \Omega(N \mid \mu) &= E - TS(E, V, N) - \mu N \\ &= F(N, V, T) - \mu N \end{aligned} \tag{78}$$

where $F(N, V, T)$ is the Helmholtz free energy, thermal equilibrium having been assumed. The tildes have now been dropped because we shall now be transforming between the two types of ensembles; $\mu$ and $N$ are independent variables with the fluctuating quantities to the left of the vertical bar and the reservoir-determined quantities on the right. Note also that here (and elsewhere) an imprecise notation is used wherein the type of the function is indicated by the form of the arguments; $\Omega(N \mid \mu)$ and $\Omega(\mu \mid N)$ are two completely different functions. The probability of this sub-system having $N$ particles is the exponential of the fluctuation potential

$$\wp(N \mid \mu) = \frac{e^{-\beta F(N, V, T)} e^{\beta \mu N}}{\Xi(\mu)} \tag{79}$$

where the partition function is

$$\Xi(\mu) = \sum_{N=0}^{\infty} e^{-\beta F(N, V, T)} e^{\beta \mu N} \tag{80}$$

The quantity that is sought is $\wp(\mu \mid N)$, which is the probability that the chemical potential of the reservoir is $\mu$, given that the sub-system has $N$ particles. Using Bayes' theorem this is

$$\wp(\mu \mid N) = \frac{\wp(N \mid \mu)\, \wp(\mu)}{\wp(N)} \tag{81}$$

where the denominator is the appropriate normalising factor. Bayes' theorem is of course the formally exact representation of compound and conditional probability, $\wp(ab \mid c) = \wp(a \mid bc)\, \wp(b \mid c) = \wp(b \mid ac)\, \wp(a \mid c)$.

The quantity $\wp()$ is the probability that the reservoir has chemical potential $\mu$, which appears to be a rather ill-defined concept. Such, however, is the nature of Bayesian *a priori* distributions, and there is nothing useful that can be added here to a debate that has continued unabated since the time of Laplace. Suffice it to say that here is assumed a uniform distribution, $\wp(\mu) = \text{const.}$, perhaps invoking Laplace's principle of insufficient reason, or else mentioning that this is the Jeffries' prior for a location parameter, $\mu \in (-\infty, \infty)$.

Retaining only the $\mu$-dependent terms, the probability distribution is

$$\wp(\mu \mid N) = \frac{e^{\beta \mu N}}{\Xi(\mu)\, Z(N)} \tag{82}$$

with

$$Z(N) = \int_{-\infty}^{\infty} d\mu\, \frac{e^{\beta \mu N}}{\Xi(\mu)} \tag{83}$$

Writing this in the form of a fluctuation potential,

$$\wp(\mu \mid N) = \frac{e^{-\beta \Omega(\mu \mid N)}}{Z(N)} \tag{84}$$

one has

$$\Omega(\mu \mid N) = -\Omega(\mu) - \mu N \tag{85}$$

which, apart from the immaterial constant $N\bar{\mu}(N)$, is precisely the result given above, Eq. (77).

Whereas the density functional has the interpretation of the fluctuation potential, or equivalently the constrained total entropy, the meaning of the activity functional is not so apparent. The difficulty is that number and density profiles are physical objects and one can readily imagine that they fluctuate. The chemical potential and the external field are well-defined mathematically, but their fluctuations are harder to visualise. Nevertheless, Bayes' theorem shows that the activity functional likewise determines the probability of such fluctuations.

## 5. CONCLUSION

Density functional theory is a powerful mathematical procedure for determining the density profile due to a specified external field. What has become confused over the years is the precise relationship between the density functional and the thermodynamic potential, and what has also become obscured is the explicit and formally exact density representation of the intrinsic Helmholtz free energy that underlies the theory. In fact such an explicit representation for the equilibrium grand potential actually predates density functional theory, as is graphically illustrated in the review of Stell.(1) The present paper proves the equivalence of the non-equilibrium density functional that utilises this explicit grand potential and the conventional implicit representation based upon the cross-entropy.

What is also done here is to maintain?throughout the distinction between equilibrium and non-equilibrium quantities. This seemingly-trivial detail is arguably responsible for much confusion in statistical mechanics, including that alluded to above concerning the relationship of the density functional to a thermodynamic potential. From a certain point of view it makes no sense to say that the free energy is minimised at equilibrium since it is arguably purely an equilibrium quantity. Accordingly, one cannot have it that the density functional is simultaneously a free energy and a variational principle for determining equilibrium.

This difficulty is resolved in general by introducing a fluctuation potential that is a function based upon the constrained total entropy, and which determines the probability of the occurrence of a non-equilibrium state.(5) The thermodynamic potential bf conventional statistical mechanics is the minimum value of the fluctuation potential. What was shown here was that the density functional as determined conventionally from the cross-entropy was in fact the fluctuation potential that was determined here from first principles; minimisation of the fluctuation potential to find the equilibrium density actually corresponded to maximising the constrained total entropy, which is the formal criterion for the equilibrium state. Because of this equivalence between the density functional, the fluctuation potential, and the constrained total entropy, it was also shown that the density functional actually gave the probability of density fluctuations of the system, and that it was unique in this regard.

## NOTE ADDED IN PROOF

An alternative activity functional to that given in the text is $\mathscr{F}(\tilde{z} \mid \rho, V, T) = \Omega(\tilde{z}, V, T) + k_B T \int d\mathbf{s}\, \rho(\mathbf{s}) \ln \Lambda^3 \tilde{z}(\mathbf{s})$, which is maximized at equilibrium where it equals the intrinsic Helmholtz free energy. An analogous result holds for the pair potential functional.

## REFERENCES

1. G. Stell, in *The Equilibrium Theory of Classical Fluids*, H. Frisch and J. L. Lebowitz, eds. (Benjamin, New York, 1964), p. II-171.
2. J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).
3. R. Evans, *Adv. Phys.* **28**:143 (1979).
4. This is true provided that the configuration probabilities are restricted to the usual Boltzmann form with fixed internal potential. It would be more precise to say that there is a one-to-one relationship between the activity (equivalently the external potential) and the density profile.
5. P. Attard, unpublished.
6. M. S. Green, *J. Math. Phys.* **1**:391 (1960).
7. F. H. Stillinger and F. P. Buff, *J. Chem. Phys.* **57**:1 (1962).
8. C. de Dominicis, *J. Math. Phys.* **3**:983 (1962); **4**:255 (1963).
9. P. Attard and G. N. Patey, *J. Chem. Phys.* **92**:4970 (1990).
10. P. Attard, *J. Chem. Phys.* **95**:4471 (1991).
11. P. Attard and S. J. Miklavic, *J. Chem. Phys.* **99**:6078 (1993).
12. W. Olivares and D. A. McQuarrie, *J. Chem. Phys.* **65**:3604 (1976).
13. T. Morita, *Prog. Theor. Phys.* **23**:839 (1960).
14. P. Attard, *Phys. Rev. A* **45**:3659 (1992).
15. P. Attard, *J. Chem. Phys.* **94**:2370 (1991).
16. H. B. Callan, *Thermodynamics* (Wiley, New York, 1960).