

III. THE ORNSTEIN-ZERNIKE EQUATION CAN BE DERIVED USING DFT

The s -body density distribution of a single component whose center of mass motion behaves classically is given as

$$n^{(s)}(\underline{r}_1 \dots \underline{r}_s) = \sum_{N=s}^{\infty} \frac{q^N}{(N-s)! \Xi} \int \dots \int e^{-\beta \left(\sum_{i>j=1}^N U_{AA}(\underline{r}_{ij}) + \sum_{i=1}^N U_{AP}(\underline{r}_i) - N\mu \right)} d^3 \underline{r}_{s+1} \dots d^3 \underline{r}_N \quad (2.1)$$

where q is the internal and kinetic energy partition function, U_{AA} is the molecular pairwise interaction potential, U_{AP} is the external potential, μ is the chemical potential, and Ξ is the grand canonical partition function, given as

$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} \frac{q^N}{N!} \int \dots \int e^{-\beta \left(\sum_{i>j=1}^N U_{AA}(\underline{r}_{ij}) + \sum_{i=1}^N U_{AP}(\underline{r}_i) - N\mu \right)} d^3 \underline{r}_1 \dots d^3 \underline{r}_N \quad (2.2)$$

For $s=1$, we have the singlet density distribution, $n^{(1)}(\underline{r})$. For $s=2$, we have the doublet density distribution, $n^{(2)}(\underline{r}, \underline{r}')$. Frequently, we prefer to deal in terms of the pair correlation function, $g^{(2)}(\underline{r}, \underline{r}')$, rather than the double density distribution. As a reminder, the relationship between them is

$$g^{(2)}(\underline{r}, \underline{r}') = \frac{n^{(2)}(\underline{r}, \underline{r}')}{n^{(1)}(\underline{r})n^{(1)}(\underline{r}')} \quad (2.3)$$

Key Point

The s -body density distribution functions can be computed as functional derivatives of the grand canonical partition function, $\Xi(T, V, \mu)$. We are going to take the functional derivative of $\Xi(T, V, \mu)$ with respect to $\phi(\underline{r})$, where

$$\phi(\underline{r}) = U_{AP}(\underline{r}) - \mu \quad (2.4)$$

so that the expression $\sum_{i=1}^N U_{AP}(\underline{r}_i) - N\mu$ in the partition function becomes

$$\sum_{i=1}^N U_{AP}(\underline{r}_i) - N\mu = \sum_{i=1}^N [U_{AP}(\underline{r}_i) - \mu] = \sum_{i=1}^N \phi(\underline{r}_i) \quad (2.5)$$

The functional derivative of the partition function is

$$\frac{\delta \Xi(\{\phi\})}{\delta \phi(\underline{r})} = \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{q^N}{N!} \int \dots \int \left(\frac{\delta e^{-\beta \left(\sum_{i>j=1}^N U_{AA}(\underline{r}_{ij}) + \sum_{i=1}^N \phi(\underline{r}_i) \right)}}{\delta \phi(\underline{r})} \right) d^3 \underline{r}_1 \dots d^3 \underline{r}_N \quad (2.6)$$

Recall that the functional derivative of a function is

$$\frac{\delta F(\{y\})}{\delta y(\underline{x})} = \frac{\delta f(y(\underline{x}), \underline{x})}{\delta y(\underline{x})} = \frac{\partial f(y(\underline{x}), \underline{x})}{\partial y(\underline{x})} \delta(\underline{x}' - \underline{x}) \quad (1.21)$$

Using equation (1.21) we can write,

$$\frac{\delta e^{-\beta \phi(\underline{r}_j)}}{\delta \phi(\underline{r})} = -\beta e^{-\beta \phi(\underline{r}_j)} \delta(\underline{r}_j - \underline{r}) \quad (2.7)$$

so that equation (2.6) becomes

$$\frac{\delta \Xi(\{\phi\})}{\delta \phi(\underline{r})} = \frac{1}{\Xi} \sum_{N=1}^{\infty} \frac{q^N}{N!} \int \dots \int e^{-\beta \left(\sum_{i>j=1}^N U_{AA}(\underline{r}_{ij}) + \sum_{i=1}^N \phi(\underline{r}_i) \right)} \left(\sum_{j=1}^N -\beta \delta(\underline{r}_j - \underline{r}) \right) d^3 \underline{r}_1 \dots d^3 \underline{r}_N \quad (2.8)$$

Note that the summation in the functional derivative of the partition function begins at $N=1$ and not $N=0$ (as it did for the partition function itself) because the $N=0$ term has no dependence on $\phi(\underline{r})$.

If the particles are identical, then the sum over j in equation 2.8 is a sum over common terms and one can replace $\sum_{j=1}^N -\beta \delta(\underline{r}_j - \underline{r}) = -N\beta \delta(\underline{r}_1 - \underline{r})$. Substituting back into equation (2.8) yields

$$\frac{\delta \Xi(\{\phi\})}{\delta \phi(\underline{r})} = -\beta \frac{1}{\Xi} \sum_{N=1}^{\infty} \frac{q^N}{(N-1)!} \int \dots \int e^{-\beta \left(\sum_{i>j=1}^N U_{AA}(\underline{r}_{ij}) + \sum_{i=1}^N \phi(\underline{r}_i) \right)} \delta(\underline{r}_1 - \underline{r}) d^3 \underline{r}_1 \dots d^3 \underline{r}_N \quad (2.9)$$

where the factor of N was absorbed into the factorial. Comparing equations (2.9) and (2.1) we find that the singlet density distribution is proportional to $\frac{\delta \Xi(\{\phi\})}{\delta \phi(\underline{r})}$

$$n^{(1)}(\underline{r}_1) = -kT \frac{\delta \Xi(\{\phi\})}{\delta \phi(\underline{r})} \quad (2.10)$$

Equation (2.10) appears to be a closed expression. However, in practice, it is not tractable since it involves the evaluation of the configuration integrals in the partition function.

We can carry out a second functional differentiation to obtain:

$$(kT)^2 \frac{\delta^2 \Xi(\{\phi\})}{\delta\phi(\underline{r})\delta\phi(\underline{r}')} = -kT \frac{\delta n(\underline{r})}{\delta\phi(\underline{r}')} = n^{(2)}(\underline{r}, \underline{r}') - n^{(1)}(\underline{r})n^{(1)}(\underline{r}') + n^{(1)}(\underline{r})\delta(\underline{r}' - \underline{r}) \quad (2.11)$$

We see that the functional derivative of the 1-body density distribution with respect to the external potential is related to the 2-body density distribution function.

In the case of no correlations, $n^{(2)}(\underline{r}, \underline{r}') = n^{(1)}(\underline{r})n^{(1)}(\underline{r}')$, so equation (2.11) becomes

$$-kT \frac{\delta n(\underline{r})}{\delta\phi(\underline{r}')} = n^{(1)}(\underline{r})\delta(\underline{r}' - \underline{r}) \quad (2.12)$$

We know from the functional differentiation that

$$\int \frac{\delta\phi(\underline{r})}{\delta n(\underline{r}'')} \frac{\delta n(\underline{r}'')}{\delta\phi(\underline{r}')} d^3 r'' = \delta(\underline{r}' - \underline{r}) \quad (1.26)$$

Combining equation (2.12) and (1.26) we have

$$-\beta \int \frac{\delta\phi(\underline{r})}{\delta n(\underline{r}'')} n^{(1)}(\underline{r}'') \delta(\underline{r}' - \underline{r}'') d^3 r'' = -\beta \frac{\delta\phi(\underline{r})}{\delta n(\underline{r}')} n^{(1)}(\underline{r}') = \delta(\underline{r}' - \underline{r}) \quad (2.13)$$

Rearranging, we have

$$\frac{\delta\phi(\underline{r})}{\delta n(\underline{r}')} = -\frac{kT}{n^{(1)}(\underline{r})} \delta(\underline{r}' - \underline{r}) \quad (2.14)$$

But, of course, we know that we do have correlations and they do affect the functional derivative. We label the part of the derivative due to correlations as $kTC^{(2)}(\underline{r}, \underline{r}')$, where $C^{(2)}(\underline{r}, \underline{r}')$ is the direct correlation function. We add this contribution to equation (2.14)

$$\frac{\delta\phi(\underline{r})}{\delta n(\underline{r}')} = -\frac{kT}{n^{(1)}(\underline{r})} \delta(\underline{r}' - \underline{r}) + kTC^{(2)}(\underline{r}, \underline{r}') \quad (2.15)$$

If we substitute equation (2.15) and equation (2.11) into equation (1.26) we have

$$\int \left[\frac{1}{n^{(1)}(\underline{r})} \delta(\underline{r}'' - \underline{r}) - C^{(2)}(\underline{r}, \underline{r}'') \right] \left[n^{(2)}(\underline{r}'', \underline{r}') - n^{(1)}(\underline{r}'')n^{(1)}(\underline{r}') + n^{(1)}(\underline{r}'')\delta(\underline{r}' - \underline{r}'') \right] d^3 r'' = \delta(\underline{r}' - \underline{r}) \quad (2.16)$$

Simplifying,

$$\begin{aligned}
& \frac{1}{n^{(1)}(\underline{r})} \left[n^{(2)}(\underline{r}, \underline{r}') - n^{(1)}(\underline{r})n^{(1)}(\underline{r}') + n^{(1)}(\underline{r})\delta(\underline{r}' - \underline{r}) \right] - C^{(2)}(\underline{r}, \underline{r}')n^{(1)}(\underline{r}') \\
& - \int C^{(2)}(\underline{r}, \underline{r}'') \left[n^{(2)}(\underline{r}'', \underline{r}') - n^{(1)}(\underline{r}'')n^{(1)}(\underline{r}') \right] d^3r'' = \delta(\underline{r}' - \underline{r}) \\
& n^{(1)}(\underline{r}') \left[g^{(2)}(\underline{r}, \underline{r}') - 1 \right] + \delta(\underline{r}' - \underline{r}) - C^{(2)}(\underline{r}, \underline{r}')n^{(1)}(\underline{r}') \\
& - \int C^{(2)}(\underline{r}, \underline{r}'') n^{(1)}(\underline{r}'') n^{(1)}(\underline{r}') \left[g^{(2)}(\underline{r}'', \underline{r}') - 1 \right] d^3r'' = \delta(\underline{r}' - \underline{r}) \\
& n^{(1)}(\underline{r}') \left[g^{(2)}(\underline{r}, \underline{r}') - 1 \right] - C^{(2)}(\underline{r}, \underline{r}')n^{(1)}(\underline{r}') - n^{(1)}(\underline{r}') \int C^{(2)}(\underline{r}, \underline{r}'') n^{(1)}(\underline{r}'') \left[g^{(2)}(\underline{r}'', \underline{r}') - 1 \right] d^3r'' = 0 \\
& \left[g^{(2)}(\underline{r}, \underline{r}') - 1 \right] - C^{(2)}(\underline{r}, \underline{r}') - \int C^{(2)}(\underline{r}, \underline{r}'') n^{(1)}(\underline{r}'') \left[g^{(2)}(\underline{r}'', \underline{r}') - 1 \right] d^3r'' = 0 \\
& g^{(2)}(\underline{r}, \underline{r}') - 1 = C^{(2)}(\underline{r}, \underline{r}') + \int C^{(2)}(\underline{r}, \underline{r}'') n^{(1)}(\underline{r}'') \left[g^{(2)}(\underline{r}'', \underline{r}') - 1 \right] d^3r'' \tag{2.17}
\end{aligned}$$

Equation (2.17) is the Ornstein-Zernike equation. It requires a closure in order to solve. Typically the closure takes the form of an approximation to the s-body density distribution in terms of the (s-1)-body density distribution.

This example was intended to show that functional calculus is just another tool one can use to deal with statistical mechanics. Note: When people talk about using DFT to find molecular distributions, they do not mean that they are solving the Ornstein-Zernike equation.