Lecture 6: Density Functional Theory

Wednesday, June 3, 2020 3:22 PM

- Introduce a field $J(r)$

- Derive a variational principle to determine $\langle \hat{\rho}(r) \rangle$

$$Z_c[J] = z_0 \int dr^N e^{-\beta U(r) - \int dr\, J(r) \hat{\rho}(r)}$$

$$= e^{-\beta A[J]}$$

If $J(r) = 0$, this is the equil. ensemble

$$-\frac{\delta \log Z_c[J]}{\delta J(r)} = \frac{1}{Z_c} z_0 \int dr^N \hat{\rho}(r) e^{-\beta U(r) - \int dr\, J(r) \hat{\rho}(r)}$$

$$= \langle \hat{\rho}(r) \rangle_J = \beta \frac{\delta A[J]}{\delta J(r)}$$

$\beta = 1$ from here on

Assume the relation b/t $J(r)$, $\langle \hat{\rho}(r) \rangle$ is invertible

If we know $\langle \hat{\rho}(r) \rangle$, we can calculate $J(r)$

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$$\frac{\delta^2 A}{\delta J(r)\,\delta J(r')} = \frac{\delta \langle \hat{\rho}(r) \rangle_J}{\delta J(r')} = -\langle \hat{\rho}(r)\,\hat{\rho}(r') \rangle$$

$\Big\downarrow$ b/c of invertible

$$\frac{\delta J(r)}{\delta \langle \hat{\rho}(r') \rangle_J} = -\langle \hat{\rho}(r)\,\hat{\rho}(r') \rangle^{-1}$$

Use Legendre transform to derive

$$F[\langle \hat{\rho} \rangle] \equiv A[J] - \int dr\, J(r)\, \underline{\frac{\delta A[J]}{\delta J(r)}}$$

$$= \underline{A[J]} - \int dr\, J(r)\, \langle \hat{\rho}(r) \rangle_J$$

$$\frac{\delta F}{\delta \langle \hat{\rho}(r) \rangle} = -J(r)$$

$$\frac{\delta^2 F}{\delta \langle \hat{\rho}(r) \rangle\, \delta \langle \hat{\rho}(r') \rangle} = -\frac{\delta J(r)}{\delta \langle \hat{\rho}(r') \rangle} = \langle \hat{\rho}(r)\,\hat{\rho}(r') \rangle^{-1}$$

- If we have $F[J]$ as a power series in $\rho(r)$, the quadratic term is related to $S(k)$

- Interactions are reflected in the form of this coefficient

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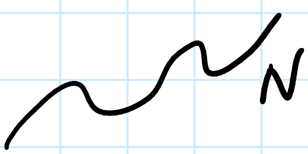
- Stability of the homogeneous phase can be assessed

- Now we use FT to calculate this quadratic coefficient

Model A / Edwards model:



$$\beta U_0 = \sum_{i}^{n} \sum_{s}^{N-1} \frac{3}{2b^2} \left| r_{i,s} - r_{i,s+1} \right|^2$$

$$\beta U_1 = \frac{u_0}{2} \int dr \left[\hat{\rho}(r)\right]^2$$

Use H-S transforms w/ the field $J(r)$ in place:

$$Z[J] = z_0 \int dr^{nN} \, e^{-\beta U_0 - \beta U_1 - \int dr \, J(r) \hat{\rho}(r)}$$

$$= Z_1 \int Dw \, e^{-H[w,J]} = e^{-A[J]}$$

$$H[w,J] = \frac{1}{2u_0} \int dr \left[w(r)\right]^2 - n \log Q[\mu]$$

$$\mu(r) = i w(r) + J(r)$$

Recall $Q[\mu] = \frac{1}{V} \int dr^{nN} e^{-\mu(r_N)} \Phi_{N,N-1} e^{-\mu(r_{N-1})} \cdots \Phi_{2,1} e^{-\mu(r_1)}$

Use the MF equation $\frac{\delta H}{\delta w} = 0$

$$\frac{\delta H}{\delta w} = \frac{1}{u_0} w(r) - i \tilde{\xi}(r; [w, J])$$

Next time, use W.I.E. on $\tilde{\xi}$ to relate $w(r)$ to $J(r)$