

Lecture 2: Particles to Fields

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Ch 3, Hanson & McDonald, Theory of Simple Liquids

§4.1, Ewald Theory of Isomop. Polymers, G. Fredrickson

Consider $n=1$ in a fixed external field

$$\hat{f}(\underline{r}) = \delta(\underline{r} - \underline{r}_j)$$

External field $\omega(\underline{r})$

$$H = K + U + W$$

$$W = \int d\underline{r} \hat{f}(\underline{r}) \omega(\underline{r}) = \int d\underline{r} \delta(\underline{r} - \underline{r}_j) \omega(\underline{r})$$

$$= \omega(\underline{r}_j)$$

$$Z = \frac{1}{n!} \int d\underline{r}_1 \int d\underline{r}_2 \dots e^{-\beta H} = \frac{1}{n! \lambda_T^3} \int d\underline{r} e^{-\beta W} \quad \text{All energies in } k_B T \quad (\beta = 1)$$

$$= \frac{1}{n! \lambda_T^3} \int d\underline{r}_j e^{-\omega(\underline{r}_j)}$$

$$Q[\omega] = \frac{1}{V} \int d\underline{r}_j e^{-\omega(\underline{r}_j)}$$

$$Z = \frac{V}{n! \lambda_T^3} Q[\omega]$$

For many particles, we have:

$$Z = \frac{1}{n! \lambda_T^{3n}} \int d\underline{r}^n e^{-U(\underline{r}^n)}$$

To calculate the local thermal average

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for systems that interact through pair potentials

$$U(\Sigma^n) = \frac{1}{2} \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n u(\Sigma_i - \Sigma_j)$$

Define the microscopic density $\hat{f}(\Sigma) = \sum_{r=1}^n f(\Sigma - \Sigma_r)$

$$U(\Sigma^n) = \frac{1}{2} \int d\Sigma \int d\Sigma' \hat{f}(\Sigma) u(\Sigma - \Sigma') \hat{f}(\Sigma') - \frac{1}{2} n u(0)$$

$$Z = \frac{1}{n! \lambda_T^{3n}} \int d\Sigma^n e^{\frac{1}{2} n u(0)} e^{-\frac{1}{2} \int d\Sigma \int d\Sigma' \hat{f}_r u_{rr'} \hat{f}_{r'}}$$
$$\hat{f}_r = \hat{f}(\Sigma)$$
$$Z_0 = \frac{e^{\frac{1}{2} u(0)}}{\lambda_T^3}$$

$$Z = \frac{Z_0^n}{n!} \int d\Sigma^n e^{-\frac{1}{2} \int d\Sigma \int d\Sigma' \hat{f}_r u_{rr'} \hat{f}_{r'}}$$

Hubbard-Stratonovich Transformation

- Assume $u(\Sigma)$ has a functional inverse $u^{-1}(\Sigma)$

$$\begin{aligned} & \exp \left(-\frac{1}{2} \int d\Sigma \int d\Sigma' \hat{f}(\Sigma) u(\Sigma - \Sigma') \hat{f}(\Sigma') \right) \\ &= \frac{\int D\omega \exp \left[-\frac{1}{2} \int d\Sigma \int d\Sigma' \omega(\Sigma) u^{-1}(\Sigma, \Sigma') \omega(\Sigma') + i \int d\Sigma \omega(\Sigma) \hat{f}(\Sigma) \right]}{\int D\omega \exp \left[-\frac{1}{2} \int d\Sigma \int d\Sigma' \omega(\Sigma) u^{-1}(\Sigma, \Sigma') \omega(\Sigma') \right]} \\ &= \Omega_0 \end{aligned}$$

Plug into Z :

$$Z = \frac{Z_0^n}{n! \Omega_0} \int D\omega \int d\zeta^n \left\{ \exp \left[-\frac{1}{2} \int d\zeta \int d\zeta' \omega(\zeta) \tilde{u}^*(\zeta, \zeta') \omega(\zeta') \right] \right.$$

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 $\times \exp \left[i \int d\zeta \omega(\zeta) \hat{g}(\zeta) \right] \right\} \quad *$

Focus on terms w/ particle coordinates:

$$\begin{aligned}
 & \int d\zeta^n \exp \left[i \int d\zeta \omega(\zeta) \hat{g}(\zeta) \right] \\
 &= \int d\zeta^n e^{i \sum_j \int d\zeta \omega(\zeta) \delta(\zeta - \zeta_j)} = \int d\zeta^n e^{i \sum_j \omega(\zeta_j)} \\
 &= \int d\zeta_1^n e^{i \omega(\zeta_1)} \cdot e^{i \omega(\zeta_2)} \cdots e^{i \omega(\zeta_n)} \\
 &= (\int d\zeta_1 e^{i \omega(\zeta_1)}) (\int d\zeta_2 e^{i \omega(\zeta_2)}) \cdots (\int d\zeta_n e^{i \omega(\zeta_n)}) \\
 &= (\int d\zeta e^{i \omega(\zeta)})^n \quad \text{use } Q[\omega] = \frac{1}{V} \int d\zeta e^{-i \omega(\zeta)} \\
 &= (V Q[\omega])^n \\
 &= V^n Q[\omega]^n \quad \text{use } x^y = e^{y \log x} \\
 &= V^n e^{n \log Q}
 \end{aligned}$$

Plug into Z :

$$Z = \frac{Z_0^n V^n}{n! \Omega_0} \int D\omega e^{-H[\omega]}$$

$$H[\omega] = \frac{1}{2} \int d\zeta \int d\zeta' \omega(\zeta) \tilde{u}^*(\zeta - \zeta') \omega(\zeta') - n \log(Q[\omega])$$

$$Q[\omega] = \frac{1}{V} \int d\zeta e^{-i \omega(\zeta)}$$

$H[\omega]$ is in general complex (e^{-H} is not pos. def.)

H = "affortis $H_{\text{real}} + i H_{\text{imag}}$ "

$H =$ "effective Hamiltonian"

Sample potentials:

$$u(r) = u_0 \delta(r) \quad u^{-1}(r) = \frac{1}{u_0} \delta(r)$$

Yukawa potential: $u(r) = \frac{u_0}{4\pi r} e^{-\lambda r}, \quad u_0 = \frac{q_i q_j}{\epsilon_0 \epsilon_r}$

$$\hat{u}(k) = \frac{u_0}{(2\pi)^3} \frac{1}{k^2 + \lambda^2}$$

$$\hat{u}^{-1}(k) = \frac{(2\pi)^3}{u_0} (k^2 + \lambda^2)$$

Limit as $\lambda \rightarrow 0^+$, we get Coulomb's law:

$$u(\Sigma - \Sigma') = \frac{u_0}{|\Sigma - \Sigma'|}$$

$$u^{-1}(\Sigma - \Sigma') = -\frac{1}{4\pi} \nabla^2 \delta(\Sigma - \Sigma')$$

Calculating Properties

Average quantities in a field theory:

$$\langle M \rangle = \frac{\int d\omega M(\omega) e^{-\beta E(\omega)}}{\int d\omega e^{-\beta E(\omega)}}$$

$$\mu = \left(\frac{\partial \Gamma}{\partial n} \right)_{V,T} = -kT \left(\frac{\partial \log Z}{\partial n} \right)_{V,T}$$

$$p = kT \left(\frac{\partial \log Z}{\partial V} \right)_{T,n} \quad U = kT^2 \left(\frac{\partial \log Z}{\partial T} \right)_{n,V}$$

For the chemical potential:

$$\mu = -kT \frac{\partial}{\partial n} \left(n \log z_0 + n \log V - \log n! - \log S_0 \right)$$

$$\mu = -kT \frac{\partial}{\partial n} \left(n \log z_0 + n \log V - \log n! - \log S_{D\omega} \right. \\ \left. + \log \left(S_{D\omega} e^{-H[\omega]} \right) \right)$$

$$= kT \log \frac{S}{z_0} + \frac{\int_{D\omega} \frac{\partial H}{\partial n} e^{-H[\omega]}}{\int_{D\omega} e^{-H[\omega]}}$$

$$= kT \log \frac{S}{z_0} + kT \langle \frac{\partial H}{\partial n} \rangle$$

$$\frac{\partial H}{\partial n} = -\log Q[\omega]$$

$$\mu = kT \log \frac{S}{z_0} - kT \langle \log Q \rangle$$

To calculate $\langle \hat{g}(\xi) \rangle$, go back to *

$$Z = \frac{z_0^n}{n! \lambda_r^{3n}} \int_{D\omega} \int_{dr} \left\{ \exp \left[-\frac{i}{2} \int_{dr} \int_{dr'} w(\xi) \bar{w}(\xi, \xi') w(\xi') \right] \right. \\ \times \left. \exp \left[i \int_{dr} w(\xi) \hat{g}(\xi) \right] \right\}$$

$$\langle \hat{g}(\xi) \rangle = \frac{\frac{z_0^n}{n! \lambda_r^{3n}} \int_{D\omega} \int_{dr} \hat{g}(\xi) e^{-\frac{i}{2} \int_{dr} \int_{dr'} w_r u_{rr'} w_r} e^{-i \int_{dr} u_r \hat{g}_r}}{Z}$$

$$= \frac{\frac{z_0^n}{n! \lambda_r^{3n}}}{Z} \int_{D\omega} \left\{ e^{-\frac{i}{2} \int_{dr} \int_{dr'} w_r u_{rr'} w_r} \cdot \left[-\frac{\delta}{\delta i w(r)} \frac{\int_{dr} e^{-i \int_{dr} w(r) \hat{g}(r)}}{e} \right] \right\} \\ = \Omega^{\eta \log Q[\omega]}$$

$$= \frac{\frac{z_0^n}{n! \lambda_r^{3n}}}{Z} \int_{D\omega} \frac{-\delta \eta \log Q[\omega]}{\delta i w(r)} \cdot e^{-H[\omega]}$$

$$Z = \sum_{\sigma} e^{-\beta E_{\sigma}} = \sum_{\sigma} e^{-\beta E_{\sigma}}$$

Density operator: $\tilde{\rho}(\Sigma; [i\omega]) = -\gamma \frac{\delta \log Q(i\omega)}{\delta i\omega(r)}$

$$\langle \tilde{\rho}(\Sigma) \rangle = \langle \hat{\rho}(\Sigma) \rangle$$

$$Q(i\omega) = \frac{1}{V} \int d\mathbf{r} e^{-i\omega r}$$

$$\frac{1}{QV} e^{-i\omega r} = \tilde{\rho}(\Sigma; [i\omega])$$

$$Z = \frac{1}{n! \lambda_r^n} \int d\mathbf{r}^n e^{-H(\mathbf{r})} = Z_1 \int d\mathbf{r} e^{-H(\mathbf{r})}$$