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CHE 528
TEST 2

2) Derive a formula that expresses the equal-time force-force correlation function in terms of the pair correlation function $g(r)$.

$$\vec{F_a} = -\nabla_a \Phi$$

$$\left\langle \vec{F_a} \cdot \vec{F_a} \right\rangle = \langle \nabla_a \Phi \cdot \nabla_a \Phi \rangle$$

$$= \frac{\displaystyle\int d\tilde{r}\, e^{-\beta\Phi}\, \nabla_a \Phi \cdot \nabla_a \Phi}{\displaystyle\int d\tilde{r}\, e^{-\beta\Phi}} = \frac{N}{D}$$

Describing the numerator, N

$$e^{-\beta\Phi}\, \nabla_a \Phi = \nabla_a (e^{-\beta\Phi} \Phi) - (\nabla_a e^{-\beta\Phi}) \Phi$$

$$fg' = (fg)' - f'g$$

$$e^{-\beta\Phi}\, \nabla_a \Phi = -\beta^{-1} \nabla_a\, e^{-\beta\Phi}$$

$$N = \int d\tilde{r} (-\beta^{-1} \nabla_a\, e^{-\beta\Phi}) \cdot \nabla_a \Phi$$

$$= -\frac{1}{\beta} \int d\tilde{r} (\nabla_a e^{-\beta\Phi} \cdot \nabla_a \Phi) = \frac{1}{\beta} \int d\tilde{r} \left[\nabla_a (e^{-\beta\Phi} \nabla_a \Phi) - e^{-\beta\Phi} \nabla_a^2 \Phi \right]$$

$$N = -\frac{1}{\beta} \int d\tilde{r}\, \nabla_a (e^{-\beta\Phi} \nabla_a \Phi) + \frac{1}{\beta} \int d\tilde{r}\, e^{-\beta\Phi}\, \nabla_a^2 \Phi$$

As $\Phi \rightarrow 0$ the first integral goes to 0. This is a surface integral.

$$\left\langle \vec{F}_a \cdot \vec{F}_a \right\rangle = \frac{1}{\beta} \left\langle \nabla_a^2 \Phi \right\rangle$$

$$\Phi = \sum_{b \neq a} u(r_{ab}) + rest$$

$$\nabla_a^2 \Phi = \sum_{b \neq a} \nabla_a^2 u(r_{ab})$$

$$\beta \left\langle \vec{F}_a \cdot \vec{F}_a \right\rangle = \sum_{b \neq a} \left\langle \nabla_a^2 u(r_{ab}) \right\rangle = \sum_{b \neq a} \left\langle \nabla_{ab}^2 u(r_{ab}) \right\rangle = (N-1) \left\langle \nabla_{ab}^2 u(r_{ab}) \right\rangle$$

$$\text{Therefore } \beta \left\langle \vec{F}_a \cdot \vec{F}_a \right\rangle = (N-1) \left\langle \nabla_{ab}^2 u(r_{ab}) \right\rangle$$

$$\text{Where } \left\langle \nabla_{ab}^2 u(r_{ab}) \right\rangle = \int d^3\vec{r_a} \int d^3\vec{r_b} \nabla_{ab}^2 u(r_{ab}) \int d^3 r_1 ... \int d^3 r_N \, \rho^N(r_1 ... r_N)$$

$$\text{Not including a or b } \int d^3 r_1 ... \int d^3 r_N \, \rho^N(r_1 ... r_N) = \rho^2(r_a r_b)$$

$$\beta \left\langle \vec{F}_a \cdot \vec{F}_a \right\rangle = \frac{N(N-1)}{N} \int dr_a \int dr_b \, \nabla_{ab}^2 u(r_{ab}) \rho^2(r_a r_b)$$

$$N(N-1)\rho^2(ab) = \rho^2 = \rho^2 g(r_{ab})$$

$$\beta \left\langle \vec{F}_a \cdot \vec{F}_a \right\rangle = \frac{\rho^2}{N} \int dr_a \int dr_b \, \nabla_{ab}^2 u(r_{ab}) g(r_{ab})$$

Transform based on relative coordinates

$$\vec{r_a}, \vec{r_b} \rightarrow \vec{r_a}, \vec{r} = \vec{r_a} - \vec{r_b}$$

$$\int d^3\vec{r_a} \int d^3\vec{r_b} = \int d^3\vec{r_a} \int d^3\vec{r}$$

$$\beta \left\langle \vec{F}_a \cdot \vec{F}_a \right\rangle = \rho^2 \frac{V}{N} \int d^3\vec{r} \, \nabla^2 u(r) \, g(r)$$

$$= 4\pi\rho \int_0^\infty dr \, r^2 \left[\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d\,u(r)}{dr} \right] g(r)$$

$$\beta \left\langle \vec{F}_a \cdot \vec{F}_a \right\rangle = 4\pi\rho \int_0^\infty dr \, \frac{d}{dr} \left[r^2 u'(r) \right] g(r)$$