DISTRIBUTION FUNCTIONS (II)

- Assume that the potential energy has the form

$$U(\bar{r}_1, \dots \bar{r}_N) = \sum_{i<j} V(\bar{r}_i - \bar{r}_j) \leftarrow \boxed{\text{pair interactions}}$$

- We can compute $\langle U \rangle$ using $g^{(2)}(r)$

$$\langle U \rangle = \sum_{i<j} \langle V(\bar{r}_i - \bar{r}_j) \rangle =$$

$$= \sum_{ij} \underbrace{\int d^3R \langle \delta(\bar{r}_i - \bar{r}_j - \bar{R})}_{\text{This integral is } 1 \text{ (nothing depends on } \bar{R})} V(\bar{r}_i - \bar{r}_j) \rangle$$

$$= \sum_{i<j} \int d^3R \langle \delta(\bar{r}_i - \bar{r}_j - \bar{R}) V(\bar{R}) \rangle$$

$$= \sum_{i<j} \int d^3R \, V(R) \langle \delta(\bar{r}_i - \bar{r}_j - R) \rangle$$

Now: there is nothing special about particles i, j

$$\langle \delta(\bar{r}_1 - \bar{r}_j - \bar{R}) \rangle = \langle \delta(\bar{r}_1 - \bar{r}_2 - R) \rangle$$

$$= \frac{1}{V^2} g^{(2)}(\bar{R})$$

volume $\rightarrow$ V

$$\langle U \rangle = \frac{1}{V} \sum_{i<j} \int d^3R \, V(R) g^{(2)}(R)$$

[Nothing depends on the links and there are $\frac{1}{2} N(N-1)$ links]

$$= \frac{1}{V} \frac{N(N-1)}{2} \int d^3R \, V(R) g^{(2)}(R)$$

$$\left[\frac{N-1}{V} \approx \frac{N}{V} = \rho\right]$$

$$\approx N \cdot \frac{\rho}{2} \int d^3R \, V(R) g^{(2)}(R)$$

[proportional to N: extensive ok]

We can compute $p^{(exc)}$ using $g^{(2)}(\bar{r})$

$$p^{exc} = -\frac{1}{3V}\sum_{i<j} \left\langle |r_{ij}| \frac{\partial V}{\partial(|r_{ij}|)} \right\rangle$$

$$= -\frac{1}{3V}\sum_{i<j} \underbrace{\int d^3R \left\langle \delta(\vec{r}_{ij} - \vec{R})\right.}_{\text{Integral} = 1} \left. |r_{ij}| \frac{\partial V}{\partial |r_{ij}|} \right\rangle$$

$$= -\frac{1}{3V}\sum_{i<j} \int d^3R\, |R| \frac{\partial V}{\partial |R|} \left\langle \delta(\bar{r}_{ij} - \bar{R}) \right\rangle$$

$$= -\frac{1}{3V^2}\sum_{i<j} \int d^3R\, |R| \frac{\partial V}{\partial |R|}\, g^{(2)}(R)$$

$$= -\frac{1}{3V^2}\,\frac{N(N-1)}{2} \int d^3R\, |R| \frac{\partial V}{\partial |R|}\, g^{(2)}(R)$$

$$= -\frac{\rho^2}{6} \int d^3R\, |R| \frac{\partial V}{\partial |R|}\, g^{(2)}(R) \qquad [\text{intensive}]$$

$$p = \rho kT - \frac{\rho^2}{6} \int d^3R\, |R| \frac{\partial V}{\partial |R|}\, g^{(2)}(R)$$

If we use that both V and $g^{(2)}$ only depend on $|R|$

$$p = \rho kT - \frac{\rho^2}{6} \cdot 4\pi \int_0^\infty dR\, R^3 \frac{\partial V}{\partial R}\, g^{(2)}(R)$$

integration over the solid angle

STRUCTURE FACTOR

$$S(\vec{q}) = \frac{1}{N}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} e^{i\bar{q}\cdot(\bar{r}_i-\bar{r}_j)} \right\rangle$$

$$= 1 + \frac{1}{N}\sum_{i\neq j}\left\langle e^{iq\cdot(\bar{r}_i-\bar{r}_j)}\right\rangle$$

terms with $i=j$

$$= 1 + \frac{1}{N}\sum_{i\neq j}\int d^3R \left\langle \delta(r_{ij}-\bar{R})\, e^{i\bar{q}\cdot\bar{r}_{ij}}\right\rangle$$

$$= 1 + \frac{1}{N}\sum_{i\neq j}\int d^3R\, \frac{1}{V}\, g^{(2)}(R)\, e^{i\bar{q}\cdot\bar{R}}$$

$$= 1 + \frac{1}{\cancel{N}}\cancel{N}(N-1)\frac{1}{V}\int d^3R\, g^{(2)}R\, e^{i\bar{q}\cdot\bar{R}}$$

$$\simeq 1 + \rho\int d^3R\, g^{(2)}(R)\, e^{i\bar{q}\cdot\bar{R}} \qquad \boxed{\frac{N-1}{V}\approx\frac{N}{V}=\rho}$$

This integral is singular since $g^{(2)}(R)\to 1$ for $|R|\to\infty$.

$$\simeq 1 + \rho\int d^3R\,(g^{(2)}(R)-1)\,e^{iq\cdot R} + \rho\int d^3R\, e^{i\bar{q}\cdot\bar{R}}$$

$$= 1 + (2\pi)^3\delta^{(3)}(\bar{q}) + \rho\int d^3R\,(g^{(2)}(R)-1)\,e^{iq\cdot R}$$

NOT RELEVANT for $\bar{q}\neq 0$

In scattering expt. $\bar{q} \propto$ transfered momentum