1 Density

1.1 Real Space, $\rho(\vec{r})$

$$
\rho(\vec{r}) = \sum_{i=1}^{N} \langle \delta(\vec{r}_i - \vec{r}) \rangle = \sum_{i=1}^{N} \frac{\Theta(\vec{r}_i \in \text{Bin}_{\vec{r}})}{\text{Vol. of Bin}_{\vec{r}}} \tag{1}
$$

$$
= \rho, \quad \text{(for uniform system)} \tag{2}
$$

In a crystal, the mean-squared deviation from a set of lattice sites $\{\vec{Z}_i\}$ is important.

$$
u^2 = < (\vec{r}_1 - \vec{z}_i)^2 > \tag{3}
$$

A classical solid melts when $u^2 > 0.15d_{nn}^2$ (Lindemann’s ratio)

1.2 $\vec{k}$ - Space, $\rho_k$

$$
\rho(\vec{k}) = \int d^3r e^{i\vec{k} \cdot \vec{r}} \rho(\vec{r}) = \sum_{i=1}^{N} e^{i\vec{k} \cdot \vec{r}_i} \tag{4}
$$

$$
\rho_0 = N \tag{5}
$$

$$
\rho_{k \neq 0} = 0, \quad \text{(for uniform system)} \tag{6}
$$

Note: In rectangular periodic boundary conditions, $\vec{k} = \left( \frac{2\pi}{L_x} n_x, \frac{2\pi}{L_y} n_y, \frac{2\pi}{L_z} n_z \right)$.

Fourier smoothing is done by removing terms that have $k > k_{\text{cut-off}}$,

$$
\tilde{\rho}(\vec{r}) = \frac{1}{\Omega} \sum_{|\vec{k}| \leq k_{\text{cut-off}}} \rho_k e^{-i\vec{k} \cdot \vec{r}} \tag{7}
$$

2 Pair Correlation

2.1 Pair Correlation Function, $g(\vec{r})$

In the following formulas, realize the definitions may only make sense for $|\vec{r}| \leq L/2$.

$$
g(\vec{r}) = \frac{2\Omega}{N^2} \sum_{i<j} \langle \delta(\vec{r}_i - \vec{r}_j - \vec{r}) \rangle \tag{8}
$$

For free particles, $g(r) = 1 - 1/N$.

Sum rule is $\int d^3rg(r) = (1 - 1/N)\Omega$.

The potential energy and the pressure estimator can be written in terms of $g(r)$,

$$
V = \left\langle \sum_{i<j} \phi(r_{ij}) \right\rangle = \frac{N\rho}{2} \int d^3r \phi(\vec{r}) g(\vec{r}) \tag{9}
$$

$$
P = \frac{k_B T}{\Omega} - \frac{\rho^2}{6} \int d^3r g(r) r \frac{d\phi}{dr} \tag{10}
$$
The tail correction for a shifted potential is:

$$\Delta V = 2\pi N \rho \left[ \phi(r_c) \int_{0}^{r_c} r^2 dr g(r) + \int_{r_c}^{\infty} r^2 dr \phi(r) \right]$$

(11)

assuming \(g(r) = 1\) for \(r > r_c\).

2.2 Structure Factor, \(S_k\)

\(S_k^* = \frac{1}{N} (\rho \rho - \rho)\)

(12)

\(S_0 = N\)

(13)

For a perfect crystal \(S_k\) will be zero almost everywhere, except for some well-defined spikes. In particular, for a bravais lattice the spikes are located at reciprocal lattice points,

\(S_k = N \sum_G \delta_{k,G}\)

(14)

In general

\(S_k = 1 + (N-1) \sum_G \delta_{k,G} e^{-k^2u^2/3}\)

(15)

where the Debye-Waller factor \(u\) is defined in Eq. (3).

For a non-perfect crystal, the spikes will soften, and in the limit \(k \to \infty\), \(S_k \to 1\).

For free particles, \(S_k = 1 + (N-1)\delta_{k,0}\).

The short-wavelength behavior of the structure factor is related to the compressibility, \(\chi_T = (\rho dP/d\rho)^{-1}\) by the relation

\[\lim_{k \to \infty} S_k = \rho k_B T \chi_T\]

(16)

2.3 Relation between \(g(r)\) and \(S_k\)

Exact formulas for periodic boundaries:

\(S_K = 1 + N \delta_{k,0} + \rho \int_{\Omega} d^3r \ e^{i \vec{r} \cdot \vec{r}} (g(\vec{r}) - 1)\)

(17)

\(g(\vec{r}) = \frac{1}{N} \sum_k e^{i \vec{k} \cdot \vec{r}} (S_K - 1)\)

(18)

Formulas assuming a large box and isotropic correlations in 3D:

\(S_k = 1 + N \delta_{k,0} + \frac{4\pi \rho}{k} \int_{0}^{\infty} dr \sin(kr)(g(r) - 1)\)

(19)

\(g(r) = 1 + \frac{1}{2\pi^2 pr} \int_{0}^{\infty} dk \sin(kr)(S_K - 1)\)

(20)

Formulas assuming a large box and isotropic correlations in 2D:

\(S_k = 1 + N \delta_{k,0} + 2\pi \rho \int_{0}^{\infty} dr J_0(kr)(g(r) - 1)\)

(21)

\(g(r) = 1 + \frac{1}{2\pi \rho} \int_{0}^{\infty} dk \ J_0(kr)(S_K - 1)\)

(22)
Please email any questions or corrections to ceperley@uic.edu