Thermodynamic Estimators

Name	Symbol	Formula	
Kinetic Energy	K	$\frac{1}{2}\sum_i m_i v_i^2$	$= \frac{1}{2}k_B T(\text{degrees of freedom})$
Potential Energy	U	$\sum_{i<j} \phi(r_{ij})$	$= \frac{N}{2}\rho \int d^3r\, \phi(r) g(r)$
Pressure	$P = -\frac{\partial F}{\partial \Omega}$	$\frac{1}{3\Omega}[2K - \sum_{i<j} r_{ij}\frac{d\phi}{dr}]$	$= \rho k_B T - \frac{\rho^2}{6}\int d^3r\, g(r) r \frac{d\phi}{dr}$
Specific Heat	$C_V = \frac{\partial F}{\partial T}$	$\frac{1}{(k_B T)^2}\langle (E - \langle E \rangle)^2 \rangle$	$= (3/2)N + \frac{1}{(k_B T)^2}[\langle V^2 \rangle - \langle V \rangle^2]$

Physical Structure Estimators

1 Density

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

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

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

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

$$u^2 =< (\mathbf{r_i} - \mathbf{z_i})^{\mathbf{2}} > \tag{3}$$

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

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

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

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

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

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

Fourier smoothing is done by removing terms that have $k > k_{cutoff}$,

$$\tilde{\rho}(\vec{r}) = \frac{1}{\Omega}\sum_{|\vec{k}|\leq k_{cutoff}} \rho_{\vec{k}} e^{-\vec{k}\cdot\vec{r}} \tag{7}$$

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 $\int d^3 r g(r) = (1 - 1/N)\Omega$.

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

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

$$P = \rho k_B T - \frac{\rho^2}{6} \int d^3 r g(r) r \frac{d\phi}{dr} \tag{10}$$

The tail correction for a shifted potential is:

$$\Delta V = 2\pi N \rho \left[\phi(r_c) \int_0^{r_c} r^2 dr\, g(r) + \int_{r_c}^{\infty} r^2 dr\, \phi(r) \right] \tag{11}$$

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

2.2 Structure Factor, S_k

$$\begin{aligned} S_{\vec{k}} &= \frac{1}{N} \langle \rho_{\vec{k}} \rho_{-\vec{k}} \rangle & (12) \\ S_0 &= N & (13) \end{aligned}$$

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,

$$S_k = N \sum_G \delta_{k,G}. \tag{14}$$

In general

$$S_k = 1 + (N-1) \sum_G \delta_{k,G} e^{-k^2 u^2/3} \tag{15}$$

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

$$\lim_{k \to \infty} S_k = \rho k_B T \chi_T \tag{16}$$

2.3 Relation between $g(r)$ and S_k.

Exact formulas for periodic boundaries:

$$S_{\vec{k}} = 1 + N\delta_{\vec{k},0} + \rho \int_\Omega d^3r\, e^{i\vec{k}\cdot\vec{r}}(g(\vec{r}) - 1) \tag{17}$$

$$g(\vec{r}) = \frac{1}{N}\sum_k e^{i\vec{k}\cdot\vec{r}}(S_{\vec{k}} - 1) \tag{18}$$

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

$$S_k = 1 + N\delta_{k,0} + \frac{4\pi\rho}{k}\int_0^\infty dr\, \sin(kr)(g(r) - 1) \tag{19}$$

$$g(r) = 1 + \frac{1}{2\pi^2\rho r}\int_0^\infty k\, dk\, \sin(kr)(S_{\vec{k}} - 1) \tag{20}$$

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

$$S_k = 1 + N\delta_{k,0} + 2\pi\rho\int_0^\infty dr\, J_0(kr)(g(r) - 1) \tag{21}$$

$$g(r) = 1 + \frac{1}{2\pi\rho}\int_0^\infty k\, dk\; J_0(kr)(S_{\vec{k}} - 1) \tag{22}$$

David Ceperley 2000.