Thermodynamic Estimators

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic Energy</td>
<td>$K$</td>
<td>$\frac{1}{2} \sum_i m_i v_i^2 = \frac{1}{2} k_B T \text{(degrees of freedom)}$</td>
</tr>
<tr>
<td>Potential Energy</td>
<td>$U$</td>
<td>$\sum_{i&lt;j} \phi(r_{ij}) = \frac{N}{2} \rho \int d^3 r \phi(r) g(r)$</td>
</tr>
<tr>
<td>Pressure</td>
<td>$P$</td>
<td>$\frac{1}{3!} [2K - \sum_{i&lt;j} r_{ij} \frac{d\phi}{dr}] = \rho k_B T - \frac{\rho^2}{6} \int d^3 r g(r) r \frac{d\phi}{dr}$</td>
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<tr>
<td>Specific Heat</td>
<td>$C_V$</td>
<td>$\frac{1}{(k_B T)^2} \langle (E - \langle E \rangle)^2 \rangle = (3/2)N + \frac{1}{(k_B T)^2} \langle (V^2) - \langle V \rangle^2 \rangle$</td>
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Physical Structure Estimators

1 Density

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

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

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

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

$$u^2 = \langle (r_i - z_i)^2 \rangle$$ (3)

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

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

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

$$\rho_{0} = N$$ (5)

$$\rho_{\vec{k}\neq0} = 0, \quad \text{(for uniform system)}$$ (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 $k > k_{cut-off}$.

$$\tilde{\rho}(\vec{r}) = \frac{1}{\Omega} \sum_{|\vec{k}| \leq k_{cut-off}} \rho_{\vec{k}} e^{-\vec{k} \cdot \vec{r}}$$ (7)
2 Pair Correlation

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

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

$$g(\vec{r}) = \frac{2\Omega}{N^2} \sum_{i<j} \langle \delta(\vec{r}_i - \vec{r}_j - \vec{r}) \rangle$$  \hspace{1cm} (8)

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

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

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

$$V = \left\langle \sum_{i<j} \phi(r_{ij}) \right\rangle = \frac{N\rho}{2} \int d^3r \phi(\vec{r}) g(\vec{r})$$  \hspace{1cm} (9)

$$P = \rho k_B T - \frac{\rho^2}{6} \int d^3r g(r) r \frac{d\phi}{dr}$$  \hspace{1cm} (10)

The tail correction for a shifted potential is:

$$\Delta V = 2\pi N\rho \left[ \phi(r_c) \int_0^{r_c} r^2 dr g(r) + \int_{r_c}^{\infty} r^2 dr \phi(r) \right]$$  \hspace{1cm} (11)

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

2.2 Structure Factor, $S_k$

$$S_k = \frac{1}{N} \left< \rho_{\vec{k}} \rho_{-\vec{k}} \right>$$  \hspace{1cm} (12)

$$S_0 = \frac{N}{N}$$  \hspace{1cm} (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,

$$S_k = N \sum_G \delta_{k,G}.$$  \hspace{1cm} (14)

In general

$$S_k = 1 + (N-1) \sum_G \delta_{k,G} e^{-k^2u^2/3}$$  \hspace{1cm} (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 $k \rightarrow \infty$, $S_k \rightarrow 1$.

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

$$\lim_{k \rightarrow \infty} S_k = \rho k_B T \chi_T$$  \hspace{1cm} (16)
2.3 Relation between $g(r)$ and $S_k$.

Exact formulas for periodic boundaries:

\[
S_k = 1 + N\delta_{k,0} + \rho \int d^3r e^{i\vec{k}\cdot\vec{r}}(g(\vec{r}) - 1) \tag{17}
\]

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

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

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

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

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

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

\[
g(r) = 1 + \frac{1}{2\pi\rho} \int_0^\infty k \, dk J_0(kr)(S_k - 1) \tag{22}
\]