Physical Validation of Properties of Small Grand Canonical Systems

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Small in macroscopic systems

Large in small systems
Surface molecules

Bulk molecules

Unwanted in simulations
Nanosystems
Nanothermodynamics

Isobaric-isothermal
- Macroscopic
  \[ G = \mu N \]
- Small system
  \[ G = \hat{\mu} N \]

Grand canonical
- Macroscopic
  \[ -pV \]
- Small system
  \[ -\hat{p}V \]
Differential

Integral
Small size contribution = excess property

Differential

\[ p = p^\infty + p^{\text{small}} \]

Integral

\[ \hat{p} = p^\infty + \hat{p}^{\text{small}} \]

\[ p = \hat{p} \]

in the macroscopic limit
## Nanothermodynamics

### Isobaric-isothermal

<table>
<thead>
<tr>
<th>Variable</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$</td>
<td>$-\left(\frac{\partial \hat{\mu}N}{\partial T}\right)_{p,N}$</td>
</tr>
<tr>
<td>$V$</td>
<td>$-\left(\frac{\partial \hat{\mu}N}{\partial T}\right)_{T,N}$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>$-\left(\frac{\partial \hat{\mu}N}{\partial T}\right)_{p,T}$</td>
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</tbody>
</table>

### Grand canonical

<table>
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<tr>
<td>$S$</td>
<td>$\left(\frac{\partial \hat{\rho}V}{\partial T}\right)_{\mu,V}$</td>
</tr>
<tr>
<td>$p$</td>
<td>$\left(\frac{\partial \hat{\rho}V}{\partial V}\right)_{\mu,T}$</td>
</tr>
<tr>
<td>$N$</td>
<td>$\left(\frac{\partial \hat{\rho}V}{\partial \mu}\right)_{V,T}$</td>
</tr>
</tbody>
</table>
Challenges

• Many simulations → time consuming

• Calculation of free energies
  – Macroscopic methods does not work for small systems
Grand canonical particle fluctuations
Connection to partition function

\[ \hat{\rho}V = k_B T \ln \Xi(\mu, V, T) \]

\[ S = \left( \frac{\partial \hat{\rho}V}{\partial T} \right)_{\mu,V} \]

\[ p = \left( \frac{\partial \hat{\rho}V}{\partial V} \right)_{\mu,T} \]

\[ N = \left( \frac{\partial \hat{\rho}V}{\partial \mu} \right)_{V,T} \]

\[ (k_B T)^2 \left( \frac{\partial^2 \ln \Xi}{\partial \mu^2} \right)_{T,V} = \langle N^2 \rangle - \langle N \rangle^2 \]
\[ \langle N^2 \rangle - \langle N \rangle^2 \]

\[ \kappa_T, C_p, V_i, H_i, G_{ij} \ldots \]
\[ \kappa_T = \frac{V}{k_B T} \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} \]

\[ = \kappa_T^\infty + \kappa_T^{\text{small}} \]

\[ \kappa_T^{\text{small}} = \frac{\Omega}{V} \kappa_T^{\text{surf}} \]
\[ \kappa_T = \kappa_T^\infty + \frac{\Omega}{V} \kappa_T^{\text{surf}} \]
Ensemble check \(^{(2)}\) = Overlapping distribution method \(^{(3)}\)

\[
\frac{1}{\beta} \ln \frac{P(N|\mu_2, T, V)}{P(N|\mu_1, T, V)} = -\Delta(pV) + \Delta\mu N
\]
\[ \hat{\rho}V = p^\infty V + \hat{\rho}^{\text{small}} V \]
\( \Delta \hat{p} \) for small systems

\( \Delta \hat{p} = \Delta p \) for reservoir

\( \hat{p} \text{small} \neq \frac{\Omega}{V} \hat{p} \text{surf} \)
Small size contributions

Surface:
\[ 6\varepsilon_{\text{surf}}(\rho, T)L^2 \]

Line:
\[ 12\varepsilon_{\text{line}}(\rho, T)L \]

Corner:
\[ 8\varepsilon_{\text{corner}}(\rho, T) \]

\[ \hat{\rho}_{\text{small}}V = 6\varepsilon_{\text{surf}}L^2 + 12\varepsilon_{\text{line}}L + 8\varepsilon_{\text{corner}} \]
\[ \Delta \hat{p}V = p^\infty V + 6L^2 \varepsilon_{\text{surf}} + 12L \varepsilon_{\text{line}} + 8 \varepsilon_{\text{corner}} \]
\( \varepsilon^{\text{surf}}, \varepsilon^{\text{line}} \) and \( \varepsilon^{\text{corner}} \) dependency on \( T \) and \( \rho \)

\[
S^{\text{small}} = \left( \frac{\partial \hat{p}^{\text{small}}}{\partial T} \right)_{\mu,V}
\]

\[
p^{\text{small}} = \left( \frac{\partial \hat{p}^{\text{small}}}{\partial V} \right)_{\mu,T}
\]

\[
N^{\text{small}} = \left( \frac{\partial \hat{p}^{\text{small}}}{\partial \mu} \right)_{V,T}
\]
Equation of State

• General in terms of:
  – Shape: , and
  – Ensemble: $\mu VT$, $NVT$ and $NpT$

• Other properties accessible from differentials

$$\kappa_T^{\text{small}} = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial p^{\text{small}}} \right)_T$$
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Thank you for your attention!