7: Common Equilibrium Calculations

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Observables and Ensemble Averages

- Variables in MD/particle-based simulation
  \[ \mathbf{r}(t) = (\mathbf{r}_1(t), \mathbf{r}_2(t), ..., \mathbf{r}_N(t)); \mathbf{p}(t) = (\mathbf{p}_1(t), \mathbf{p}_2(t), ..., \mathbf{p}_N(t)) \]
  - What we really are interested in is some (macroscopic) observable, \( O = O(\mathbf{r}(t), \mathbf{p}(t)) \)
  - How to obtain?
    - Ensemble Average
      - Average over all possible values of \( \mathbf{r}(t) \) and \( \mathbf{p}(t) \); given \( f^N(\mathbf{r}, \mathbf{p}) \)
        \[ \overline{O}(\mathbf{r}, \mathbf{p}) = \langle O \rangle_{_{\text{ens}}} = \int \int O(\mathbf{r}, \mathbf{p}) f^N(\mathbf{r}, \mathbf{p}) d\mathbf{r} d\mathbf{p} \]
    - In MD practice
      \[ \overline{O}(\mathbf{r}, \mathbf{p}, t_{\text{obs}}) = \langle O \rangle_{_{\text{time}}} = \lim_{t_{\text{obs}} \to \infty} \frac{1}{t_{\text{obs}}} \int_0^{t_{\text{obs}}} O(\mathbf{r}(t), \mathbf{p}(t)) dt \]
    - Note for Ergodic systems
      - Simulation big/long “enough”? \( \langle O \rangle_{_{\text{time}}} = \langle O \rangle_{_{\text{ens}}} \)
Thermodynamic Averages

• Calculated by LAMMPS `compute(s)`
  – Useful simulation diagnostic

• Temperature – `compute temp`
  – Equipartition of energy
    \[
    \langle K \rangle = \left\langle \sum_{i=1}^{N} \frac{p_i^2}{2m_i} \right\rangle = \frac{3}{2} Nk_B T
    \]
  – Instantaneous kinetic temperature
    \[
    \mathcal{T}(t) = \frac{1}{3Nk_B} \sum_{i=1}^{N} \frac{p_i^2(t)}{m_i}
    \]

• Not the thermodynamic temperature
Thermodynamics Averages

• **Pressure** – compute pressure
  – Kinetic (ideal) part + potential (nonideal or excess) part

\[ PV = Nk_B T + \langle W \rangle \]

  – Virial equation

\[ W = \frac{1}{3} \sum_{i=1}^{N} r_i \cdot f_i \]

  – Instantaneous

\[ P(t) = \rho k_B T(t) + W(t)/V \]

• Not the thermodynamic pressure

• **Pressure or Stress Tensor**

\[ \sigma_{\alpha\beta} = \left\langle \frac{1}{V} \sum_{i=1}^{N} \left[ \sum_{j \neq i} r_i^\alpha f_{ij}^\beta \frac{1}{2} + m_i v_i^\alpha v_j^\beta \right] \right\rangle \]
Fluctuations

- Particle simulations give more than averages
  - Statistical information is available too!
    - Fluctuations and (spatial/temporal) Correlations

- Fluctuations in (macro) observables are of interest
  \[ \delta A_{obs} = A_{obs} - \langle A \rangle_{ens} \]
  - Example: fluctuations in thermodynamic quantities
    - Specific heats
    - Coefficient of thermal expansion
    - Isothermal compressibility
Thermodynamic Fluctuations

- Specific Heat via Thermodynamic Fluctuation Theory
  - See, e.g., Landau and Lifshitz (1980) *Statistical Physics*
    \[ \langle \delta E^2 \rangle = k_B T^2 C_v \]

- In MD practice (e.g., Allen and Tildesley, *Computer Simulation of Liquids*)
  \[ \langle \delta E^2 \rangle = \langle \delta H^2 \rangle_{NVT} = \langle \delta K^2 \rangle_{NVT} + \langle \delta U^2 \rangle_{NVT} \]

- Recall from equipartition
  \[ \langle \delta K^2 \rangle_{NVT} = \frac{3N}{2} (k_B T)^2 \]
  \[ \langle \delta U^2 \rangle_{NVT} = k_B T^2 \left( C_v - \frac{3}{2} N k_B \right) \]

- Isothermal Compressibility
  \[ \langle \delta V^2 \rangle_{NPT} = V k_B T \beta_T \]
Structural Quantities

• **Correlation Functions** – compute $\text{rdf}$

  – Pair correlation and Radial Distribution Function (RDF), $g(r)$

• **Usefulness**
  
  – Ensemble average of any pair function may be expressed using $g(r)$
  
    » Density, energy, pressure, chemical potential

\[
\left\langle \frac{1}{N} \sum_i \sum_{j \neq i} \delta(r - r_j + r_i) \right\rangle = \rho g(r)
\]

\[
P = \rho k_B T + \frac{2 \pi \rho^2}{3} \int \frac{dU(r)}{dr} g(r) r^3 dr
\]

• **Measurable via radiation-scattering**
Structural Quantities (cont.)

– Structure Factor

\[ S(k) = N^{-1} \langle \rho(k) \rho(-k) \rangle \quad \rho(k) = \sum_{i=1}^{N} \exp[ik \cdot r_i] \]

\[ S(k) = 1 + 4\pi \rho \int_{0}^{\infty} r^2 \frac{\sin(kr)}{kr} g(r) dr \]

– Intermediate Scattering Function

\[ I(k,t) = N^{-1} \langle \rho(k,t) \rho(-k,0) \rangle \]

• Van Hove function

Hansen and McDonald, Theory of Simple Liquids
Temporal Correlation Functions

• Relation to transport coefficients
  – Linear Response Theory (Green-Kubo)
    • Diffusion
      \[ D = \frac{1}{3} \int_0^\infty \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(t') \rangle dt' \]
    • Shear Viscosity – compute \( p_{xy} \), fix \( f_{xy} \) ave/correlate
      \[ j_{\alpha\beta}(t) = \frac{1}{V} \sum_{i=1}^{N} \left[ \sum_{j \neq i} r_{ij}^\alpha(t) f_{ij}^\beta(t) \right] + m_i v_i^\alpha(t) v_j^\beta(t) \]
      \[ \eta = \frac{V}{k_B T} \int_0^\infty \langle j_{\alpha\beta}(t) \cdot j_{\alpha\beta}(t') \rangle dt' \]
    • Bulk Viscosity
    • Thermal conductivity

• Others, e.g. orientation correlations, etc.

• Also useful in non-equilibrium settings

Zwanzig, R., Nonequilibrium Statistical Mechanics
Einstein Relations

- **Diffusion** – compute msd

\[
2Dt = \frac{1}{3} \left\langle \left| \mathbf{r}_i(t) - \mathbf{r}_i(0) \right|^2 \right\rangle
\]


- **Viscosity**

\[
2\eta t = \frac{V}{k_BT} \left\langle \left( Q_{\alpha\beta}(t) - Q_{\alpha\beta}(0) \right)^2 \right\rangle
\]

\[
Q_{\alpha\beta} = \frac{1}{V} \sum_i r_i^\alpha p_i^\beta
\]

– See LAMMPS How to section 6.21 for various viscosity techniques