

CE 530 Molecular Simulation

Lecture 6 Statistical Mechanics

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Statistical Mechanics

- Theoretical basis for derivation of macroscopic behaviors from microscopic origins
- Two fundamental postulates of equilibrium statistical mechanics
 - *microstates of equal energy are equally likely*
 - *time average is equivalent to ensemble average*
- Formalism extends postulates to more useful situations
 - *thermal, mechanical, and/or chemical equilibrium with reservoirs systems at constant T, P, and/or μ*
 - *yields new formulas for probabilities of microstates*
derivation invokes thermodynamic limit of very large system
- Macroscopic observables given as a weighted sum over microstates
 - *dynamic properties require additional formalism*

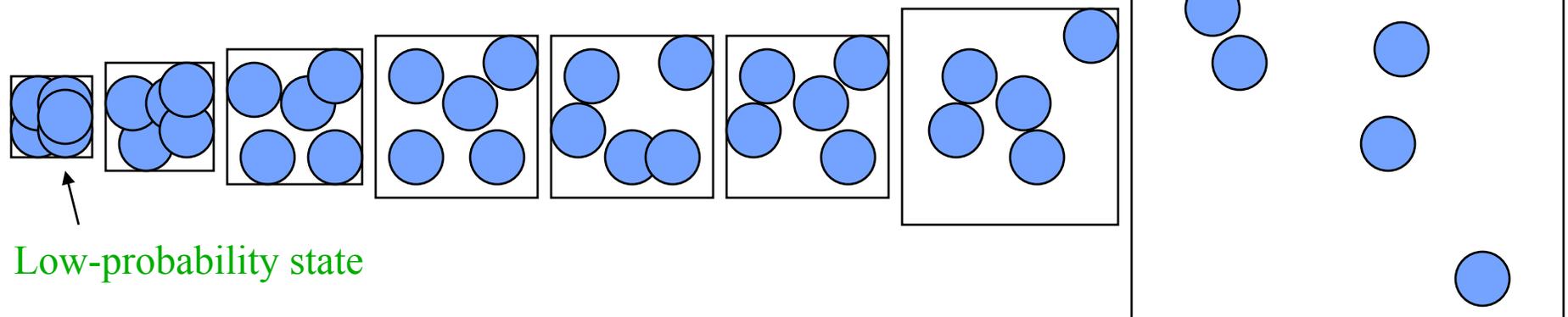
Ensembles

○ Definition of an ensemble

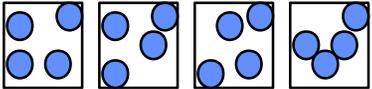
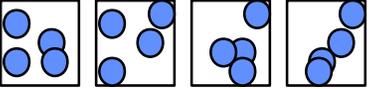
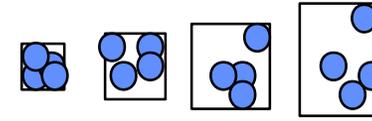
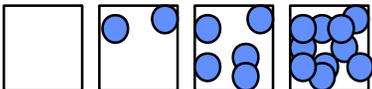
- *Collection of microstates subject to at least one extensive constraint*
 “microstate” is specification of all atom positions and momenta
 fixed total energy, total volume, and/or total number of molecules
 unconstrained extensive quantities are represented by full range of possible values
- *Probability distribution π describing the likelihood of observing each state, or the weight that each state has in ensemble average*

○ Example: Some members of ensemble of fixed N

- *isothermal-isobaric (TPN)*
 all energies and volumes represented



Commonly Encountered Ensembles

Name	All states of:	Probability distribution	Schematic
Microcanonical (EVN)	given EVN	$\pi_i = \frac{1}{\Omega}$	
Canonical (TVN)	all energies	$\pi(E_i) = \frac{1}{Q} e^{-\beta E_i}$	
Isothermal-isobaric (TPN)	all energies and volumes	$\pi(E_i, V_i) = \frac{1}{\Delta} e^{-\beta(E_i + PV_i)}$	
Grand-canonical (TVμ)	all energies and molecule numbers	$\pi(E_i, N_i) = \frac{1}{\Xi} e^{-\beta(E_i + \mu N_i)}$	

Note: $\beta \equiv 1/kT$

Partition Functions

- The normalization constants of the probability distributions are physically significant
 - *known as the partition function*
 - *relates to a corresponding free energy, or thermodynamic potential, via a bridge equation*

Ensemble	Thermodynamic Potential	Partition Function	Bridge Equation
Microcanonical	Entropy, S	$\Omega = \sum 1$	$S/k = \ln \Omega(E, V, N)$
Canonical	Helmholtz, A	$Q = \sum e^{-\beta E_i}$	$-\beta A = \ln Q(T, V, N)$
Isothermal-isobaric	Gibbs, G	$\Delta = \sum e^{-\beta(E_i + PV_i)}$	$-\beta G = \ln \Delta(T, P, N)$
Grand-canonical	Hill, L = -PV	$\Xi = \sum e^{-\beta(E_i - \mu N_i)}$	$\beta PV = \ln \Xi(T, V, \mu)$

Ensemble and Time Averaging

○ Configuration given by all positions and momenta

- “phase space” $(\mathbf{p}^N, \mathbf{r}^N) \in \Gamma$ r^N shorthand for “positions of all N atoms”

○ Configuration variable $A(\mathbf{r}^N, \mathbf{p}^N)$

○ Ensemble average

- *Weighted sum over all members of ensemble*
- *In general $\langle A \rangle = \sum A_i \pi_i$*
- *For example, canonical ensemble, classical mechanics:*

$$\langle A \rangle = \frac{1}{Q} \frac{1}{h^{3N} N!} \int dp^N \int dr^N A(p^N, r^N) e^{-\beta E(p^N, r^N)}$$

○ Time average

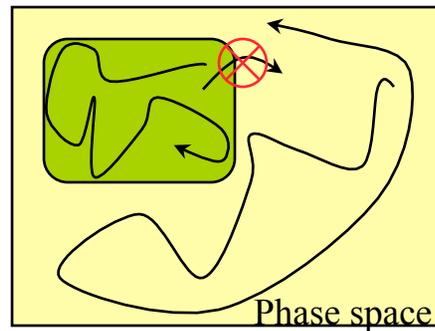
- *Sum over all states encountered in dynamical trajectory of system*

$$\bar{A} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t A \left(\underbrace{p^N(t), r^N(t)}_{\text{Given by equations of motion}}; \underbrace{p^N(0), r^N(0)}_{\text{Should average over initial conditions}} \right) dt'$$

Given by equations of motion

Ergodicity

- If a time average does not give complete representation of full ensemble, system is non-ergodic
 - *Truly nonergodic: no way there from here*
 - *Practically nonergodic: very hard to find route from here to there*



- Term applies to any algorithm that purports to generate a representative set of configurations from the ensemble
- [Click here](#) for an applet describing ergodicity.

Separation of the Energy

- Total energy is sum of kinetic and potential parts

- $E(p^N, r^N) = K(p^N) + U(r^N)$

- Kinetic energy is quadratic in momenta

- $K(p^N) = \sum_i p_i^2 / 2m_i$

- Kinetic contribution can be treated analytically in partition function

$$Q = \frac{1}{h^{3N} N!} \int dp^N e^{-\beta \sum p_i^2 / 2m} \int dr^N e^{-\beta U(r^N)}$$

$$= \frac{1}{\Lambda^{3N}} \left[\frac{1}{N!} \int dr^N e^{-\beta U(r^N)} \right]$$

$$= \frac{1}{\Lambda^{3N}} Z_N \leftarrow \text{configuration integral}$$

thermal de Broglie wavelength

$$\Lambda = \frac{h}{\sqrt{2\pi mkT}}$$

- And it drops out of position averages

$$\langle A \rangle = \frac{1}{Z_N} \frac{1}{N!} \int dr^N A(r^N) e^{-\beta U(r^N)}$$

Simple Averages 1. Energy

○ Average energy

$$\langle E \rangle = \frac{1}{Q} \frac{1}{h^{3N} N!} \int dp^N \int dr^N E(p^N, r^N) e^{-\beta E(p^N, r^N)}$$

○ Note thermodynamic connection

$$\langle E \rangle = - \frac{\partial \ln Q}{\partial \beta} = \frac{\partial (A/kT)}{\partial (1/kT)} = E_{\text{internal}}$$

definition of Q; calculus

bridge equation

Gibbs-Helmholtz equation

○ Average kinetic energy

$$\begin{aligned} \langle K \rangle &= \frac{1}{h^{3N}} \int dp^N \sum \frac{p_i^2}{2m} e^{-\beta \sum p_i^2 / 2m} \\ &= \frac{3}{2} NkT \end{aligned}$$

Equipartition of energy: $kT/2$ for each degree of freedom

○ Average potential energy

$$\langle U \rangle = \frac{1}{Z_N} \frac{1}{N!} \int dr^N U(r^N) e^{-\beta U(r^N)}$$

Simple Averages 2. Temperature

- Need to measure temperature in microcanonical ensemble (NVE) simulations
- Define instantaneous kinetic temperature

$$T = \frac{1}{3Nk} \sum p_i^2 / m$$

More generally, divide by number of molecular degrees of freedom instead of 3N

- Thermodynamic temperature is then given as ensemble average

$$T = \langle T \rangle$$

- Relies on equipartition as developed in canonical ensemble
- A better formulation has been developed recently

Simple Averages 3a. Pressure

- From thermodynamics and bridge equation

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T,N} = kT \frac{\partial}{\partial V} \ln \left[\frac{1}{N!} \int dr^N e^{-\beta U(r^N)} \right]$$

- Volume appears in limits of integration

- *Scale coordinates to move volume dependence into the potential*

$$s_k \equiv r_k / L \quad \begin{array}{l} r \in (0, L) \\ s \in (0, 1) \end{array} \quad U(r_{1x}, r_{1y}, \dots, r_{Nz}) = U(Ls_{1x}, Ls_{1y}, \dots, Ls_{Nz}) = U((Vs)^N)$$

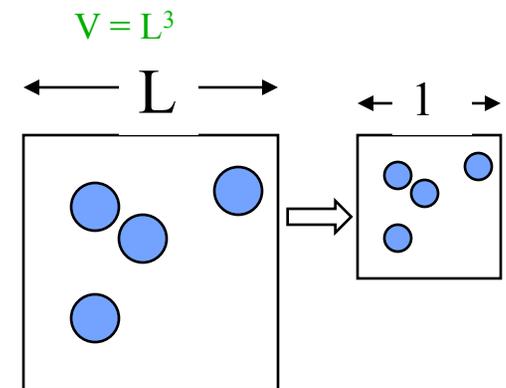
$$P = kT \frac{\partial}{\partial V} \ln \left[\frac{V^N}{N!} \int ds^N e^{-\beta U((Vs)^N)} \right]$$

- *L-derivative of U is related to force*

$$\frac{\partial}{\partial L} U((sL)^N) = \sum \frac{\partial(s_k L)}{\partial L} \frac{\partial U}{\partial(s_k L)} = -\frac{1}{L} \sum r_k f_k$$

- Result

$$P = \frac{NkT}{V} + \frac{1}{3V} \left\langle \sum_{\text{pairs } i,j} \vec{r}_{ij} \cdot \vec{f}_{ij} \right\rangle$$



Simple Averages 3b. Hard-Sphere Pressure

- Force is zero except at collision
- Time integration of virial over instant of collision is finite
 - *contribution over instant of collision*

$$\begin{aligned}\vec{r}_{12} \cdot \vec{f}_{12} dt &= \vec{r}_{12} \cdot \Delta \vec{p} \\ &= \frac{2m_1 m_2}{m_1 + m_2} \vec{v}_{12} \cdot \vec{r}_{12}\end{aligned}$$

- Pressure is sum over collisions

$$P = \frac{NkT}{V} + \frac{1}{3V} \frac{1}{t} \sum_{\text{sim collisions}} m_R \vec{v}_{12} \cdot \vec{r}_{12}$$

Simple Averages 4. Heat Capacity

- Example of a “2nd derivative” property

$$C_v = \left(\frac{\partial E}{\partial T} \right)_{V,N} = -k\beta^2 \left(\frac{\partial^2 (\beta A)}{\partial \beta^2} \right)_{V,N}$$

$$= -k\beta^2 \frac{\partial}{\partial \beta} \frac{1}{Q(\beta)} \int dr^N dp^N E e^{-\beta E}$$

- Expressible in terms of fluctuations of the energy

$$C_v = k\beta^2 \left[\langle E^2 \rangle - \langle E \rangle^2 \right]$$

Note: difference between two $O(N^2)$ quantities to give a quantity of $O(N)$

- Other 2nd-derivative or “fluctuation” properties

- *isothermal compressibility* $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N}$

(Not) Simple Averages 5. Free Energy

- Free energy given as partition-function integral

$$\begin{aligned} e^{-\beta A} &= Q \\ &= \frac{1}{h^{3N} N!} \int dp^N dr^N e^{-\beta E} \end{aligned}$$

- Impossible to evaluate

- *Even numerically!*
- *[Click here](#) for an applet demonstrating the difficulty*

- Free energy involves properties of entire ensemble

- *No value associated with a single member of ensemble*
- *For example, the size of (number of members in) the ensemble*

- The trick is to settle for computing free-energy differences

- Return to this topic later in course

Fluctuations

○ How complete is the mean as a statistic of ensemble behavior?

- *Are there many members of the ensemble that have properties that deviate substantially from the mean?*
- *Look at the standard deviation σ*

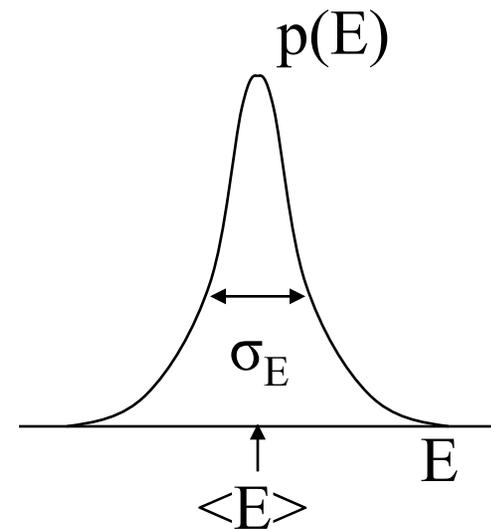
$$\sigma_E = \left\langle (E - \langle E \rangle)^2 \right\rangle^{1/2} = \left[\langle E^2 \rangle - \langle E \rangle^2 \right]^{1/2}$$

- *This relates to the heat capacity*

$$\sigma_E = kT(C_V / k)^{1/2}$$

- *Relative to mean is the important measure*

$$\frac{\sigma_E}{\langle E \rangle} = \frac{kT(C_V / k)^{1/2}}{\langle E \rangle} = \frac{O(N^{1/2})}{O(N)} = O(N^{-1/2})$$



○ Fluctuations vanish in thermodynamic limit $N \rightarrow \infty$

○ Similar measures apply in other ensembles

- *volume fluctuations in NPT; molecule-number fluctuations in μVT*

○ [Click here](#) for an applet illustrating fluctuations