Outline

* Introduction – need for statistical thermo
* Probability & statistics concepts review
* Kinetic theory example
* Statistical thermodynamics
  ✓ Postulates of statistical thermo
  ✓ Properties derived from NVE, NVT, \( \mu VT \) and PVT ensembles
  ✓ Examples: Ideal gas, monatomic crystal
  ✓ Stat. mech. of classical (vs. quantum) systems
* Useful simulation concepts
  ✓ Ergodicity
  ✓ Interaction potentials and simulating bulk materials
Limitations of Quantum Methods

∗ Semi-empirical MO does not model induced dipoles well → best for intramolecular effects
∗ Semi-empirical MO limited to hundreds of atoms
∗ Ab initio models electronic interactions well (including induced dipoles) but limited to tens of atoms due to computational cost
∗ Consequences: quantum methods are best for isolated molecules or small clusters
∗ Molecules in vacuum by default, but solvation can be modeled (e.g. COSMO)
∗ CME/MSE → interested in collective behavior
Statistical Mechanics

* “Traditional” thermodynamics: macroscopic
  ✓ Energy conservation (1st law)
  ✓ Entropy production (2nd law)
  ✓ Theory of nonideal mixtures, phase diagrams, etc.

* Stat. Mech. links microscopic & macroscopic
  ✓ Molecular interpretation of macro. measurements
  ✓ Macroscopic implications of interatomic interactions
  ✓ Answers questions of *why* phenomena observed

* Most mature for systems at equilibrium
* (Nonequilibrium extensions later)
Review of Probability

* Statistical mechanics / molecular simulations use statistics of large number of particles
* To interpret and develop ideas, use probability
* Probability defined for large number of “trials” $N$
* Discrete case: finite number of “states” $i$

$$P_i = \lim_{N \to \infty} \frac{N_i}{N}$$

Where $N_i =$ no. times state $i$ observed

* Normalization:

$$\sum_{\text{State} i} P_i = 1$$

* Average values of a function, $A(i)$

$$\langle A \rangle = \frac{1}{N} \sum_i N_i A(i) = \sum_i P_i A(i)$$

If probability of states known, any property can be calculated
Review of Probability (2)

* Fluctuations also of great importance
  \[ \delta A(i) = A(i) - \langle A \rangle \]

  \[ \langle \delta A \rangle = \sum_i P_i (A(i) - \langle A \rangle) = \sum_i P_i A(i) - \langle A \rangle \sum_i P_i = \langle A \rangle - \langle A \rangle = 0 \]

* Variance (\(\sigma\)) very useful:
  \[ \sigma_A^2 = \langle (\delta A)^2 \rangle = \sum_i P_i (A(i) - \langle A \rangle)^2 \]

  \[ = \sum_i P_i A(i)^2 - 2\langle A \rangle \sum_i P_i A(i) + \langle A \rangle^2 \sum P_i \]

  \[ = \langle A^2 \rangle - 2\langle A \rangle^2 + \langle A \rangle^2 = \langle A^2 \rangle - \langle A \rangle^2 \geq 0 \]
Review of Probability (3)

* If “state” $X_i$ is continuous, define probability density

$$f(X_i) dX_i = \frac{dN_i}{N}$$

Where $dN_i$ = no. times state between $X_i$ and $X_i + \Delta X_i$ observed

* Probability defined over intervals

$$P(X_1 \rightarrow X_2) = \int_{X_1}^{X_2} f(X_i) dX_i$$

* Averaging:

$$\langle A \rangle = \int A(X_i) f(X_i) dX_i$$

* Gaussian distribution common

$$f_G(X) = \frac{1}{\sqrt{2\pi\sigma_X^2}} \exp \left[-\frac{(X - \langle X \rangle)^2}{2\sigma_X^2}\right] \quad -\infty \leq X \leq \infty$$

Standard deviation $\sim$ width of Gaussian distribution
Kinetic Theory Example

* Consider \( N \) molecules of mass \( m \) in box, length \( l \)
* Calculate pressure = force/area on walls
* Assume elastic collisions with walls – example x-direction

* Wall in x-direction: momentum change = \( 2mv_{nx} \)
* Force = \( \Delta p/\Delta t \) where \( \Delta t \) = time between collisions = \( l/v_{nx} \)

\[
F_n = \frac{2mv_{nx}}{\Delta t} = \frac{2mv_{nx}^2}{l}
\]

* Similar magnitude of force in y and z directions
Kinetic Theory Example (2)

* Pressure exerted by n\textsuperscript{th} particle =

\[
P_n = \frac{\text{force}}{\text{area}} = \frac{2m}{l} (v_{n_x}^2 + v_{n_y}^2 + v_{n_z}^2) / 6l^2 = \frac{mv_n^2}{3V}
\]

* For N particles

\[
P = \frac{m}{3V} \sum_i v_n^2 = \frac{mN}{3V} \langle v^2 \rangle
\]

* Since speeds continuous,

\[
\langle v^2 \rangle = \int_0^\infty v^2 f(v)dv
\]

* Average translational kinetic energy:

\[
\langle U_{\text{trans}} \rangle = N \int_0^\infty \frac{m}{2} v^2 f(v)dv = \frac{N}{2} m \langle v^2 \rangle = \frac{mN}{2} \left( \frac{3PV}{mN} \right) = \frac{3}{2} PV
\]

* From ideal gas law,

\[
\langle U_{\text{trans}} \rangle = \frac{3}{2} Nk_BT
\]
Quantum or classical?

★ At atomic level, energy is quantized \( \mathcal{H}|i\rangle = E_i|i\rangle \)

★ Implications important only for certain cases

★ Will usually employ classical approximation
  ✔ Lump electronic effects into continuum interatomic potential functions (~continuous energy levels)
  ✔ Do this for both molecular fluids and solids (but potential energy functions different)
  ✔ Must parameterize to find constants
  ✔ Data from spectroscopy, phase diagram, AFM, etc.
  ✔ Valid for large number of weakly interacting particle

★ We use quantum derivation when simpler
Postulates of Statistical Mechanics

* Equal *a priori* probabilities
  - All configurations with same energy assumed to occur with *equal probability*
  - A given energy level usually is *degenerate*

* Ergodic hypothesis
  - Averaging over time = “ensemble averaging”
    - Ensemble: replicas of system, each with same specifications but different configurations
    - Specifications determine type of ensemble e.g. for canonical ensemble, NVT
  - Any configuration can be reached from another
  - For simulations, not guaranteed - must check!
Implications of Postulates

* For simplicity, consider quantum state $|i\rangle$
  Schrödinger eqn: $\mathcal{H}|i\rangle = E_i|i\rangle$ ($\mathcal{H}$ is the Hamiltonian)
* Degeneracy = No. states w/ $E_i = \Omega(N,V,E_i)$
* NVE specified = microcanonical ensemble
* Divide into two subsystems w/ $E = E_1 + E_2$
* Choose $E_1$ to maximize $\Omega$ (most likely)

$$
\ln \Omega(E_1, E_2) = \ln \Omega_1(E_1) \Omega_2(E_2) = \ln \Omega_1(E_1) + \ln \Omega_2(E - E_1)
$$

$$
\frac{\partial \ln \Omega(E_1, E - E_1)}{\partial E_1}_{N,V,E} = 0 \iff \left( \frac{\partial \ln \Omega_1(E_1)}{\partial E_1} \right)_{N_1,V_1} = \left( \frac{\partial \ln \Omega_2(E_2)}{\partial E_2} \right)_{N_2,V_2} \equiv \beta
$$

* Next, assume that $S(N,V,E) \equiv k_B \ln \Omega(N,V,E)$
Microcanonical Ensemble

- N isolated systems, each with N particles, volume V (rigid walls) and energy E
- Configuration of each different
- Interested in limit as N approaches infinity
Implications of Postulates (2)

* For meaning of $\beta$, borrow $T$ def. from thermo:

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N,V} = k_B \left( \frac{\partial \ln \Omega(E,V,N)}{\partial E} \right)_{N,V} \implies \beta = 1/(k_B T)$$

* Now, move to **canonical ensemble** (NVT)

* Small subsystem in contact with large heat bath
do that $E = E_i+E_B$ and $E_B = (E-E_i) \sim$ constant

Prob. of observing state proportional to degeneracy, so:

$$P_i = \frac{\Omega_B(E-E_i)}{\sum_j \Omega_B(E-E_j)}$$

Expanding about $E_i=0$:

$$\ln \Omega_B(E-E_i) = \ln \Omega_B(E) - E_i \frac{\partial \ln \Omega_B(E)}{\partial E} + O(1/E) \implies$$

$$\frac{\Omega_B(E-E_i)}{\Omega_B(E)} \equiv \exp(-E_i/k_BT) \implies \text{BOLTZMANN DISTRIBUTION}$$

$$P_i = \frac{\exp(-E_i/k_BT)}{\sum_j \exp(-E_j/k_BT)}$$
Canonical Ensemble

- N closed systems, each with N particles, volume V (rigid walls) at temperature T
- Configuration of each different
- Interested in limit as N approaches infinity
Relation to Macroscopic Variables

* Knowing energy distribution, average of any property \( A \) from values at states

\[
\langle A \rangle = \sum_i A_i P_i = \frac{\sum_i A_i \exp(-E_i/k_BT)}{\sum_i \exp(-E_i/k_BT)}
\]

* Bulk properties directly or from each other

* Average energy:

\[
\langle E \rangle = \frac{\sum_i E_i \exp(-E_i/k_BT)}{\sum_i \exp(-E_i/k_BT)} = -\frac{\partial \ln Q}{\partial (1/k_BT)}
\]

where \( Q = \) (canonical) partition function

* \( Q \) defined by states or by energy levels

\[
Q = \sum_{\text{states}} \exp(-E_i/k_BT) = \sum_{\text{levels}} \Omega_i \exp(-E_i/k_BT)
\]
Other Properties from Thermo

* Helmoltz free energy, $F$, related to $Q$:

$$
\langle E \rangle = \frac{\partial (F/T)}{\partial (1/T)} \quad \implies \quad F = -k_B T \ln Q
$$

* By relating $Q$ to Helmhotlz free energy, other thermodynamic properties can be derived:

$$
S = -\left( \frac{\partial F}{\partial T} \right)_{N,V} = k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q
$$

$$
p = -\left( \frac{\partial F}{\partial V} \right)_{N,T} = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T}
$$

$$
\mu_i = \left( \frac{\partial F}{\partial N_i} \right)_{T,V,N_{j\neq i}} = -k_B T \left( \frac{\partial \ln Q}{\partial N_i} \right)_{T,V,N_{j\neq i}}
$$

* Statistical thermo: find $Q$, derive all else

* This turns out to be impossible in simulations
Ideal Monatomic Gas

* For N indistinguishable, independent molecules,
  \[ Q = \frac{1}{N!} q^N \]  (assuming each molecule in different state)
* Where \( q \) = partition function of single molecule
* Particle in 3D box energies:
  \[ \varepsilon_{l_x l_y l_z} = \frac{h^2 (l_x^2 + l_y^2 + l_z^2)}{8mL^2} \]
* Density of states w/ energy < \( \varepsilon \):
  \[ \Phi(\varepsilon) = \frac{\pi}{6} \left( \frac{8m}\hbar^2 \right)^{3/2} L^3 \]
* No. states \( \varepsilon \) to \( \varepsilon + d\varepsilon \):
  \[ \omega(\varepsilon) d\varepsilon = \frac{d\Phi}{d\varepsilon} d\varepsilon = \frac{\pi}{4} \left( \frac{8m}{\hbar^2} \right)^{3/2} V \varepsilon^{1/2} d\varepsilon \]

Figure © 1986 T. L. Hill, from An Introduction to Statistical Mechanics, Dover, p. 75.
Ideal Monatomic Gas (2)

* Approximate energy levels as continuous

\[ q = \sum_{l_x,l_y,l_z=1}^{\infty} \exp(-\epsilon_{l_x,l_y,l_z}/k_B T) \equiv \int_0^\infty \omega(\epsilon) e^{-\epsilon/k_B T} d\epsilon = V / \Lambda^3 \]

\[ \Lambda = \sqrt{\frac{h^2}{2\pi mk_B T}} = \text{de Broglie wavelength} \]

* Now can easily calculate partition function

\[ Q = \frac{1}{N! \Lambda^{3N}} V^N \]

* And arrive at macroscopic EOS for pressure

\[ \langle p \rangle = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N} = Nk_B T \left( \frac{\partial \ln q}{\partial V} \right)_T = \frac{Nk_B T}{V} \]

* Can find many other functions:

\[ \mu = -k_B T \left( \frac{\partial \ln Q}{\partial N} \right)_{T,V} \approx -k_B T \ln(q / N) = -k_B T \ln(V / N\Lambda^3) \]
Ideal Monatomic Crystal

* A. Einstein – independent atoms close to equilibrium lattice positions, harmonic potentials

* Reasonable approximation at low temperature

\[ u(r) = u(0) + (1/2) f r^2 + \cdots \]

* Because particles are independent,

\[ Q(N,V,T) = \left\{ e^{-u(0)/2k_B T} \right\}^N q(V/N,T)^{3N} \]

* Energy levels for harmonic potential are

\[ \varepsilon_n = (n + 1/2) \hbar \nu \quad \quad \nu = \sqrt{f/m} / 2\pi \]
Ideal Monatomic Crystal (2)

* So,
\[
q = \sum_{n=0}^{\infty} e^{-\varepsilon_n/k_B T} = e^{-h\nu/2k_B T} \sum_{n=0}^{\infty} \left( e^{-h\nu/k_B T} \right)^n = \frac{e^{-\Theta/2T}}{1 - e^{-\Theta/T}}
\]
\[
\Theta = \frac{h\nu}{k_B}
\]

* Therefore,
\[
Q = e^{-Nu(0)/2k_B T} \left( \frac{e^{-\Theta/2T}}{1 - e^{-\Theta/T}} \right)^3
\]

* Other thermo. variables: Helmholtz free energy
\[
F = -k_B T \ln Q = Nu(0)/2 - 3Nk_B T \ln \left( \frac{e^{-\Theta/2T}}{1 - e^{-\Theta/T}} \right)
\]
Monatomic Crystal Results

* Average energy

\[
E = -k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} = -\Theta k_B \left( \frac{\partial \ln Q}{\partial (\Theta/T)} \right)_{N,V}
\]

\[
= Nu(0)/2 + 3Nh\nu / 2 + 3NkT \left( \frac{\Theta/T}{e^{\Theta/T} - 1} \right)
\]

✓ Low temperature \( E \rightarrow Nu(0)/2 + 3Nh\nu / 2 \)

✓ High temperature \( E \rightarrow 3Nk_B T \)

* Heat capacity:

\[
C_V = \left( \frac{\partial E}{\partial T} \right)_{N,V} = 3Nk \left( \frac{\Theta}{T} \right)^2 \frac{e^{\Theta/T}}{(e^{\Theta/T} - 1)^2}
\]

High T: \( C_V \rightarrow 3Nk_B \) \quad Low T: \( C_V \rightarrow 3Nk_B \left( \frac{\Theta}{T} \right)^2 e^{-\Theta/T} \)
Grand Canonical Ensemble

* N (semi)permeable systems, each with N particles, volume V & chemical potential $\mu$

$$\mu_i = \left( \frac{\partial F}{\partial N_i} \right)_{V,T,N_{j\neq i}} = \left( \frac{\partial G}{\partial N_i} \right)_{P,T,N_{j\neq i}} = -T \left( \frac{\partial S}{\partial N_i} \right)_{E,V,N_{j\neq i}}$$
Grand Canonical Ensemble

* Subsystems are open; only $\mu, V, T$ fixed
* Can derive grand partition function $\Xi$

$$\Xi(\mu, V, T) = \sum_{N=1}^{\infty} \sum_i \exp(-E_i/k_B T) \exp(N\mu/k_B T)$$

$$= \sum_{N=1}^{\infty} Q(N,V,T) \exp(N\mu/k_B T)$$

* Probability of observing state $i$ with $N$ particles:

$$P_i(N; \mu, V, T) = \frac{\exp(-E_i(N,V)/k_B T) \exp(N\mu/k_B T)}{\Xi}$$

* One can derive for entropy: $S = -k_BT \sum_{i,N} P_i(N) \ln P_i(N)$

so,

$$S = \frac{\langle E \rangle}{T} - \frac{\langle N \rangle \mu}{T} + k_B \ln \Xi = \frac{E}{T} - \frac{N\mu}{T} + \frac{pV}{T}$$

and

$$pV = kT \ln \Xi(\mu, V, T)$$

* These and other ensembles chosen for props.
Closed systems, but compressible and thermally conductive: constant $N, p, T$

$$\Delta(N, p, T) = \sum_{E_i, V_j} \exp(-E_i/k_BT) \exp(-pV_j/k_BT)$$

$$P_i(V; N, p, T) = \frac{\exp(-E_i(N, V)/k_BT) \exp(-pV/k_BT)}{\Delta}$$
Fluctuations

* If property can be evaluated instantaneously, can determine fluctuations, and more properties

* For instance, Heat Capacity:

\[
C_V = \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{N,V}
\]

\[
\frac{\partial}{\partial T} \langle E \rangle \sum e^{-E_i / k_B T} = \frac{\partial}{\partial T} \sum E_i e^{-E_i / k_B T}
\]

\[
\langle E \rangle \sum \frac{E_i}{k_B T^2} e^{-E_i / k_B T} + \frac{\partial \langle E \rangle}{\partial T} \sum e^{-E_i / k_B T} = \sum \frac{E_i^2}{k_B T^2} e^{-E_i / k_B T}
\]

\[
\frac{\partial \langle E \rangle}{\partial T} = C_V = \frac{1}{k_B T^2} \left[ \sum E_i^2 e^{-E_i / k_B T} - \langle E \rangle \sum E_i e^{-E_i / k_B T} \right] = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}
\]
Classical Statistical Mechanics

* Frenkel and Smit : quantum treatment
* We know that we lack computational resources to solve Schrödinger eqn. for N particles
* Instead of energies found as eigenvalues of the Hamiltonian of the system, use classical:

\[ \mathcal{H}_{cl} = \mathcal{K} + \mathcal{U} = \frac{1}{2m} \sum_{j=1}^{N} (p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2) + \mathcal{U}_N(x_1, ..., z_N) \]

* For partition function, replace \( \varepsilon_i \) with \( \mathcal{H}_{cl} \)
* Integrate over all momenta and positions
* Particles are indistinguishable, so divide by N!
Classical Statistical Mechanics (2)

* Divide by $h$ (Planck’s constant) for each momentum/position pair (consistent with Heisenberg uncertainty principle)

* For $N$ particles with momenta $\mathbf{p}$ and positions $\mathbf{r}$ and dimensionality $d$, 

$$Q_{\text{classical}} = \text{Tr} \exp(-\beta H) = \frac{1}{h^{dN}N!} \int d\mathbf{p}^N d\mathbf{r}^N \exp\left\{ - \beta \left( \frac{p_i^2}{2m_i} + U(\mathbf{r}^N) \right) \right\}$$

$$\langle A \rangle = \frac{\int d\mathbf{p}^N d\mathbf{r}^N \exp\left\{ - \beta \left[ \sum_i p_i^2/(2m_i) + U(\mathbf{r}^N) \right] \right\} A(\mathbf{p}^N,\mathbf{r}^N)}{\int d\mathbf{p}^N d\mathbf{r}^N \exp\left\{ - \beta \left[ \sum_i p_i^2/(2m_i) + U(\mathbf{r}^N) \right] \right\}}$$

* Terms involving momentum can be solved if $m$ is constant for all particles in 3D:

$$\int_{-\infty}^{\infty} d\mathbf{p}^N \exp(-\beta p_{ia}^2/2m_i) = \left[\int_{-\infty}^{\infty} dp \exp(-\beta p^2/2m)\right]^{3N} = (2\pi mk_B T)^{3N/2}$$

* Substituting,

$$Q_{\text{classical}} = \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N \exp\{-\beta U(\mathbf{r}^N)\}$$

* In general, energy expressed as sum, so if

$$\varepsilon = \varepsilon_{\text{trans}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{elec}}$$

* Internal contributions can be separated out

$$q = \sum e^{-\beta (\varepsilon_{\text{trans}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{elec}})} = q_{\text{trans}} q_{\text{vib}} q_{\text{rot}} q_{\text{elec}}$$
Ideal Gas Test

* For ideal gas, molecules don’t interact $\mathcal{U}=0$

$$Q_{\text{classical}} = \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N (1) = \frac{V^N}{\Lambda^{3N} N!}$$

* Agrees with quantum result (3D box)

* Can derive velocity probability density by separating out potential energy

$$f (\mathbf{v}) d\mathbf{v} = \frac{\exp(-\beta m [v_x^2 + v_y^2 + v_z^2]/2) dv_x dv_y dv_z}{\left[ \int_{-\infty}^{\infty} dv \exp (-\beta mv^2/2) \right]^{3N}}$$

$$= \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp(-\beta m [v_x^2 + v_y^2 + v_z^2]/2) dv_x dv_y dv_z$$
Simulations: Preliminary Details
Ergodic Hypothesis

* True ensemble averaging: each realization is independent and unique
* Simulations: almost always evolve in “time”
* Molecular dynamics: Solve equations of motion

\[
\bar{A} = \lim_{t \to \infty} \frac{1}{t} \int_0^t dt'A[p(t),r(t)]
\]

* If a large number of initial conditions sampled,

\[
\bar{A}(r) = \frac{\sum \lim_{t \to \infty} \frac{1}{t} \int_0^t dt'A[r;p(0),r(0),t']}\text{ No. init conditions}
\]

\[
= \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' \langle A[r;p(0),r(0),t'] \rangle_{NVE} = \langle A(r) \rangle_{NVE}
\]
Ergodicity Pitfalls

- Monte Carlo ensemble based, but in practice, also traces trajectories in *phase space*
- Must avoid loops, inaccessible regions
- Some methods developed to avoid problems

Figure  © M.P. Allen and D.J. Tildesley 1987, from *Computer Simulation of Liquids*, Oxford U. Press p. 36
Interaction Potentials

* Can go beyond classically solvable problems (ideal gases, harmonic solids)
  \[ \mathcal{H}(\mathbf{r}, \mathbf{p}) = \mathcal{K}(\mathbf{p}) + \mathcal{U}(\mathbf{r}) \]

* Kinetic energy always the same
  \[ \mathcal{K} = \sum_{i=1}^{N} \sum_{\alpha} p_{i\alpha}^2 / 2m_i \]
  where \( i \) is particle number and \( \alpha \) is coordinate

* Heart of models are interaction potentials
  \[ \mathcal{U} = \sum_i \mathcal{U}_1(\mathbf{r}_i) + \sum_i \sum_{j>i} \mathcal{U}_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_i \sum_{j>i} \sum_{k>j>i} \mathcal{U}_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \]

* \( \mathcal{U}_1 \): External field

* \( \mathcal{U}_2 \) : Pairwise interactions (most important)

* \( \mathcal{U}_3 \) : Three-body potentials (better, but costly)
Common Pair Potentials

* Hard sphere
  ✓ Purely repulsive
  \[ u^{HS}(r) = \begin{cases} \infty & (r < \sigma) \\ 0 & (r \geq \sigma) \end{cases} \]

* Square well
  ✓ Idealized minimum
  \[ u^{SW}(r) = \begin{cases} \infty & (r < \sigma_1) \\ -\varepsilon & (\sigma_2 \leq r < \sigma_1) \\ 0 & (r \geq \sigma_2) \end{cases} \]

* Soft sphere
  ✓ Continuous, repulsive
  \[ u^{SS}(r) = ar^{-\nu} \]

* Lennard-Jones (most widely used)
  \[ u^{LJ}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]
More Complex Pair Potentials

* Coulombic
  ✓ Ionic systems, unusually long-range

\[ u_{zz}(r_{ij}) = \frac{z_i z_j}{4\pi\varepsilon_0 r_{ij}} \]
  Permittivity of free space

* Molecules
  ✓ United atoms for rigid units (e.g. CH₂)
  ✓ Maybe pairwise potentials with rigid bonds
  ✓ Partial charges at one point or throughout
  ✓ Harmonic, rotational internal degrees of freedom?

* Lattice or continuum?
  ✓ Lattice much faster; continuum more accurate
  ✓ Lattices limit internal degrees of freedom (polymers)
Small Systems: Boundaries?

* Want to simulate large sample (bulk fluids)
* Limited to thousands of atoms
* Use periodic boundary conditions
  
  ✓ Box must be large enough to prevent interference ($L \sim 6\sigma$ for LJ)
  
  ✓ Can consider boxes other than square
  
  ✓ Potentials usually cut off to save time, prevent particle “feeling” itself ($\sim 2.5\sigma$ for LJ)

Replicas of system at each boundary

Particle leaving one side emerges on other

Particles “feel” phantom images from across box