

CME 599 / MSE 620 Fall 2008  
Statistical Thermodynamics and  
Introductory Simulation Concepts

S.E. Rankin

Associate Professor

Chemical and Materials Engineering

University of Kentucky, Lexington

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# 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”  $i$

$$P_i = \lim_{N \rightarrow \infty} \frac{N_i}{N} \quad \text{Where } N_i = \text{no. times state } i \text{ observed}$$

- \* 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:

$$\begin{aligned} \sigma_A^2 &= \langle (\delta A)^2 \rangle = \sum_i P_i (A(i) - \langle A \rangle)^2 \\ &= \sum_i P_i A(i)^2 - 2\langle A \rangle \sum_i P_i A(i) + \langle A \rangle^2 \sum_i P_i \\ &= \langle A^2 \rangle - 2\langle A \rangle^2 + \langle A \rangle^2 = \langle A^2 \rangle - \langle A \rangle^2 \geq 0 \end{aligned}$$

# 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:

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

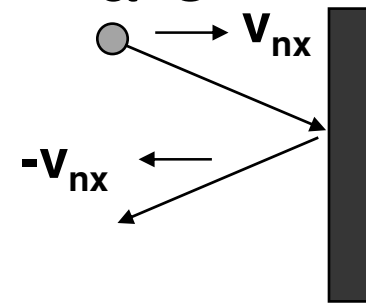
- \* Gaussian distribution common

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

**Standard deviation ~ 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  $n^{\text{th}}$  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,  $\langle U_{\text{trans}} \rangle = \frac{3}{2} Nk_B T$

# 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 particles
- \* 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/  $E = E_1 + E_2$

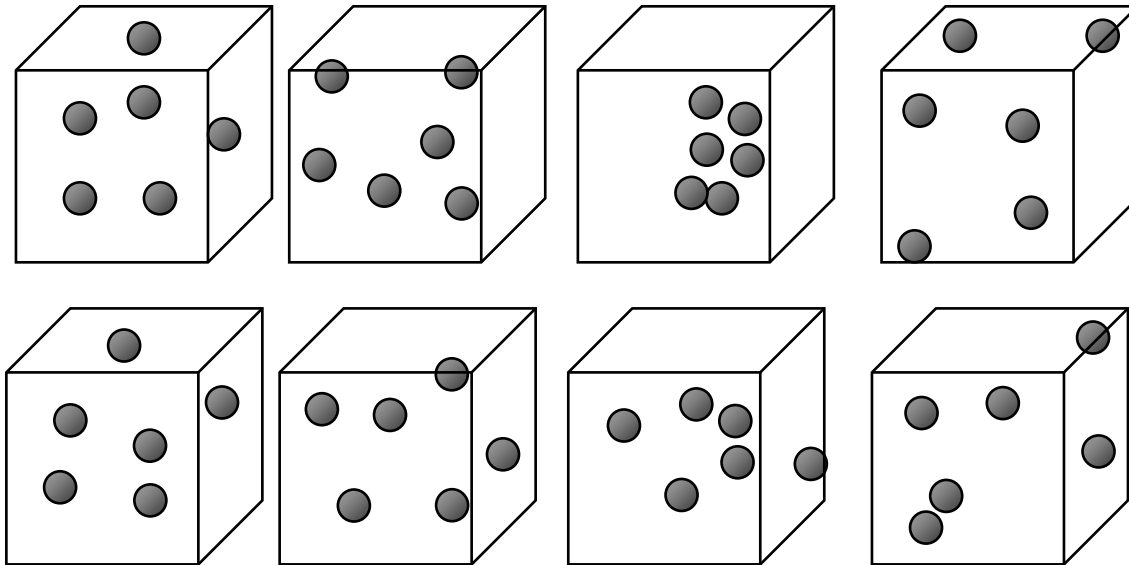
\* Choose  $E_1$  to maximize  $\Omega$  (most likely)

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

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

\* 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  
so that  $E = E_i + E_B$  and  $E_B = (E - E_i) \sim \text{constant}$

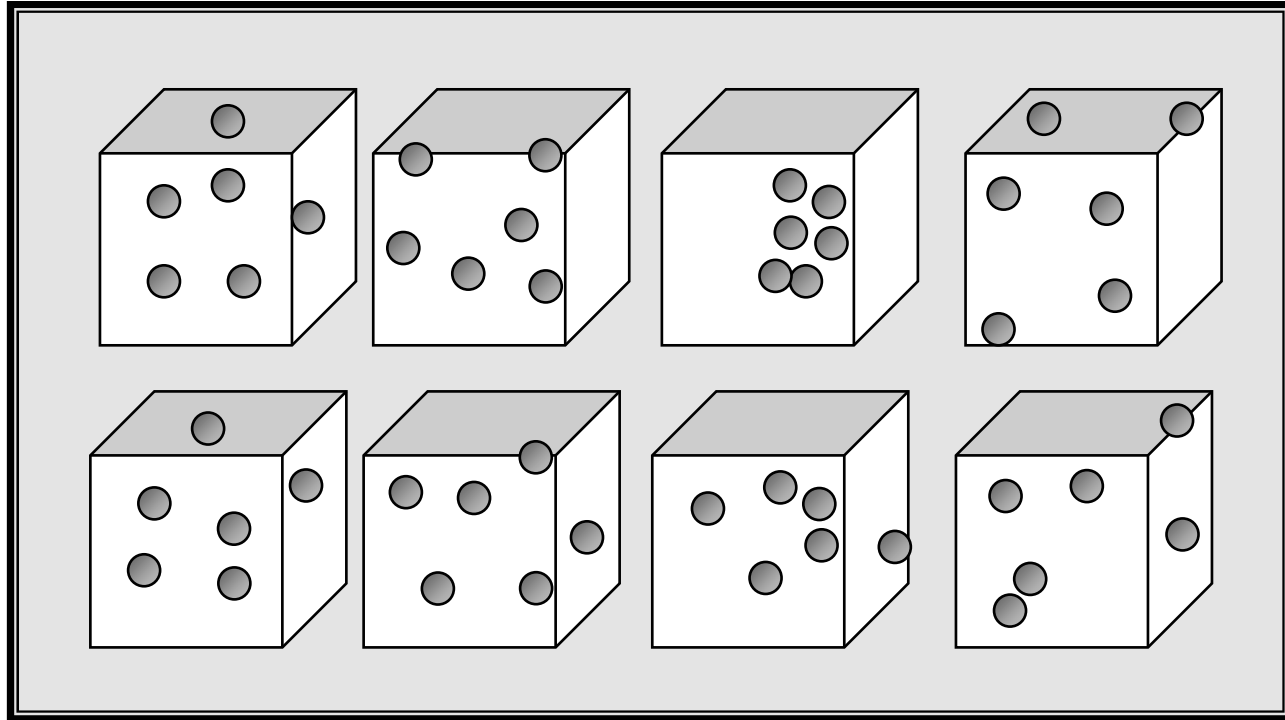
Prob. of observing state proportional to degeneracy, so:  $P_i = \frac{\Omega_B(E - E_i)}{\sum_j \Omega_B(E - E_j)}$

Expanding about  $E_i=0$ :

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

$$\frac{\Omega_B(E - E_i)}{\Omega_B(E)} \cong \exp(-E_i/k_B T) \implies \text{BOLTZMANN DISTRIBUTION} \quad P_i = \frac{\exp(-E_i/k_B T)}{\sum_j \exp(-E_j/k_B T)}$$

# 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

$$\langle A \rangle = \sum_i A_i P_i = \frac{\sum_i A_i \exp(-E_i/k_B T)}{\sum_i \exp(-E_i/k_B T)}$$

- \* Bulk properties directly or from each other

- \* Average energy:  $\langle E \rangle = \frac{\sum_i E_i \exp(-E_i/k_B T)}{\sum_i \exp(-E_i/k_B T)} = -\frac{\partial \ln Q}{\partial (1/k_B T)}$

where  $Q$  = (canonical) partition function

- \*  $Q$  defined by states or by energy levels

$$Q = \sum_{\text{states}} \exp(-E_i/k_B T) = \sum_{\text{levels}} \Omega_i \exp(-E_i/k_B T)$$

# Other Properties from Thermo

- \* Helmholtz free energy,  $F$ , related to  $Q$ :

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

- \* By relating  $Q$  to Helmholtz 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,

$$Q = \frac{1}{N!} q^N \quad (\text{assuming each molecule in different state})$$

- \* Where q = partition function of single molecule

- \* Particle in 3D box energies:

$$\epsilon_{l_x l_y l_z} = \frac{h^2(l_x^2 + l_y^2 + l_z^2)}{8mL^2}$$

- \* Density of states w/ energy <  $\epsilon$ :

$$\Phi(\epsilon) = \frac{\pi}{6} \left( \frac{8m\epsilon}{h^2} \right)^{3/2} L^3$$

- \* No. states  $\epsilon$  to  $\epsilon + d\epsilon$ :

$$\omega(\epsilon)d\epsilon = \frac{d\Phi}{d\epsilon} d\epsilon = \frac{\pi}{4} \left( \frac{8m}{h^2} \right)^{3/2} V \epsilon^{1/2} d\epsilon$$

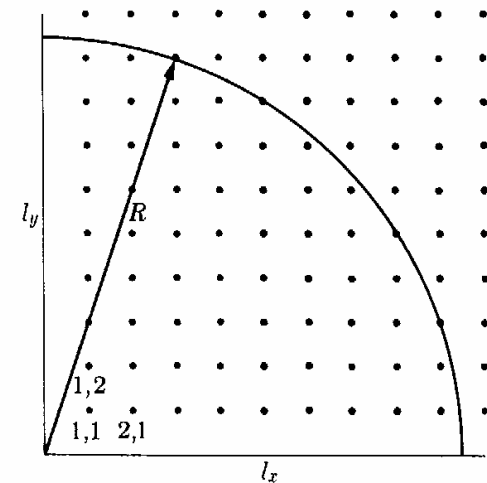


Figure © 1986 T. L. Hill, from *An Introduction to Statistical Mechanics*, Dover, p. 75.

# Ideal Monatomic Gas (2)

- \* Approximate energy levels as continuous

$$q = \sum_{l_x, l_y, l_z=1}^{\infty} \exp(-\varepsilon_{l_x l_y l_z} / k_B T) \cong \int_0^{\infty} \omega(\varepsilon) e^{-\varepsilon / k_B T} d\varepsilon = V / \Lambda^3$$

$$\Lambda = \sqrt{h^2 / 2\pi m k_B T} = \text{de Broglie wavelength}$$

- \* Now can easily calculate partition function

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

- \* And arrive at macroscopic EOS for pressure

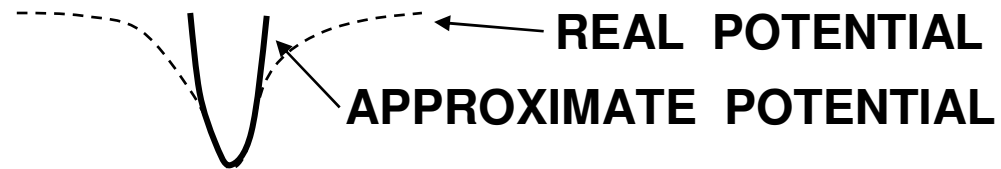
$$\langle p \rangle = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{T, N} = N k_B T \left( \frac{\partial \ln q}{\partial V} \right)_T = \frac{N k_B T}{V}$$

- \* 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



$$u(r) = u(0) + (1/2)fr^2 + \dots$$

- \* 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

$$\varepsilon_n = (n + 1/2)h\nu \qquad \nu = \frac{\sqrt{f/m}}{2\pi}$$

# 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,  $Q = e^{-Nu(0)/2k_B T} \left( \frac{e^{-\Theta/2T}}{1 - e^{-\Theta/T}} \right)^{3N}$

\* 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  $E \rightarrow Nu(0)/2 + 3Nh\nu/2$

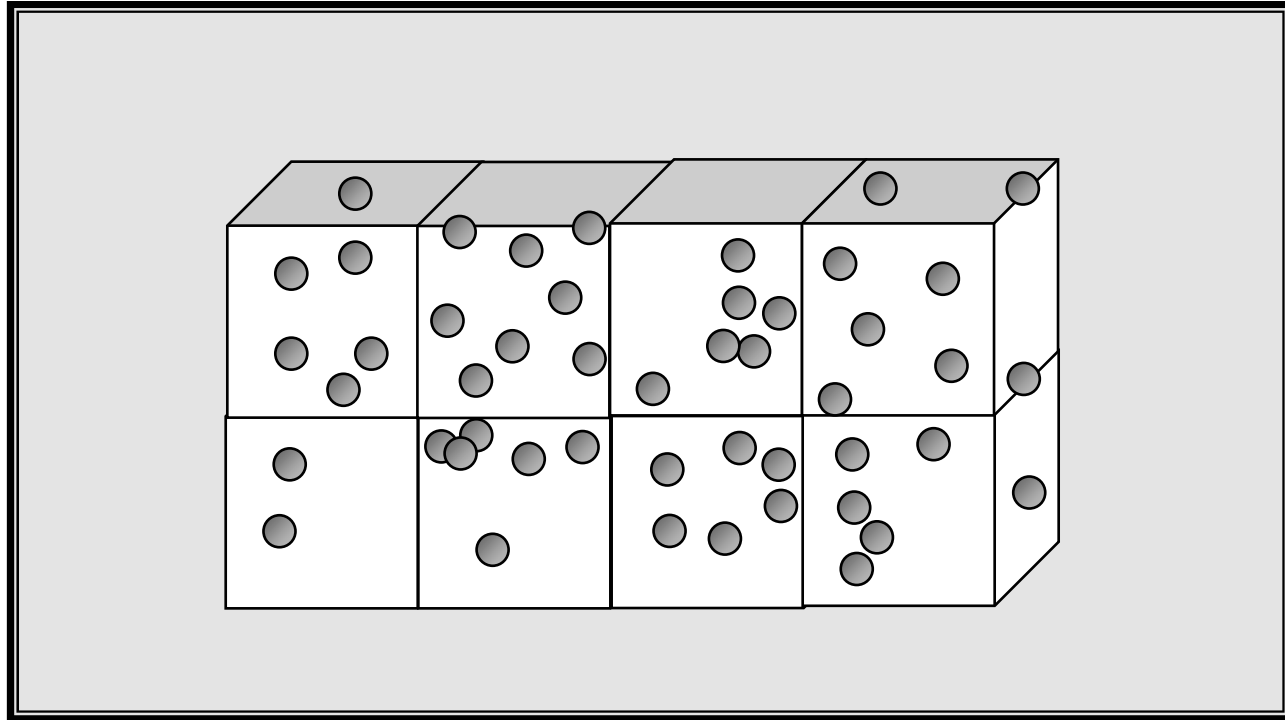
✓ High temperature  $E \rightarrow 3Nk_B T$

## \* 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:**  $C_V \rightarrow 3Nk_B$       **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  $\Xi$

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

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

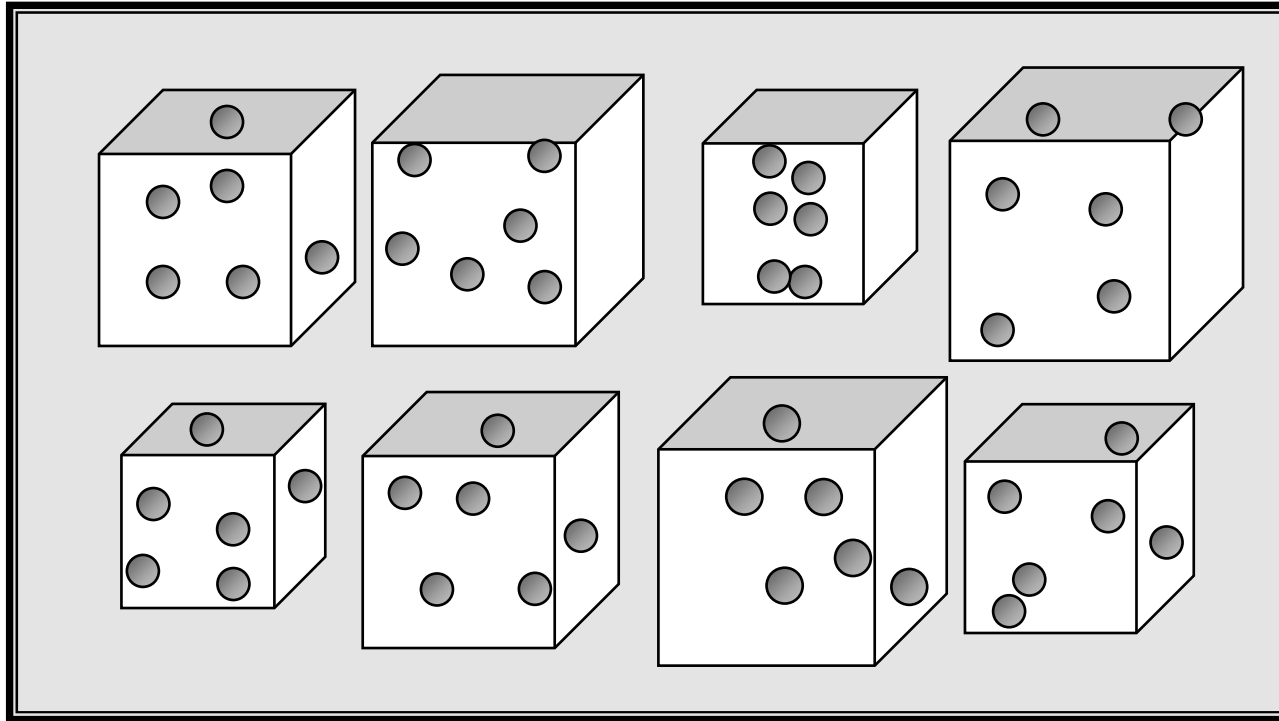
$$P_i(N; \mu, V, T) = \frac{\exp(-E_i(N, V)/k_B T) \exp(N\mu/k_B T)}{\Xi}$$

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

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.

# Isobaric Ensemble



\* Closed systems, but compressible and thermally conductive: constant  $N, p, T$

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

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

# Fluctuations

- \* If property can be evaluated instantaneously, can determine fluctuations, and more properties
- \* For instance, Heat Capacity:

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

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

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

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

# 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:

$$\mathcal{H}_{cl} = \mathcal{K} + \mathcal{U} = \frac{1}{2m} \sum_{j=1}^N (p_{x_j}^2 + p_{y_j}^2 + p_{z_j}^2) + \mathcal{U}_N(x_1, \dots, z_N)$$

- \* 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  $d$ ,

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

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

# Classical Stat. Mech. (3)

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

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

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

- \* In general, energy expressed as sum, so if

$$\mathcal{E} = \mathcal{E}_{trans} + \mathcal{E}_{vib} + \mathcal{E}_{rot} + \mathcal{E}_{elec}$$

- \* Internal contributions can be separated out

$$q = \sum e^{-\beta(\mathcal{E}_{trans} + \mathcal{E}_{vib} + \mathcal{E}_{rot} + \mathcal{E}_{elec})} = q_{trans} q_{vib} q_{rot} q_{elec}$$

# Ideal Gas Test

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

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

- \* Agrees with quantum result (3D box)
- \* Can derive velocity probability density by separating out potential energy

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

# 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

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

- \* If a large number of initial conditions sampled,

$$\overline{A(r)} = \frac{\sum_{\text{initial conditions}} \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt' A[r; \mathbf{p}(0), \mathbf{r}(0), t']}{\text{No. init conditions}}$$

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

# 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

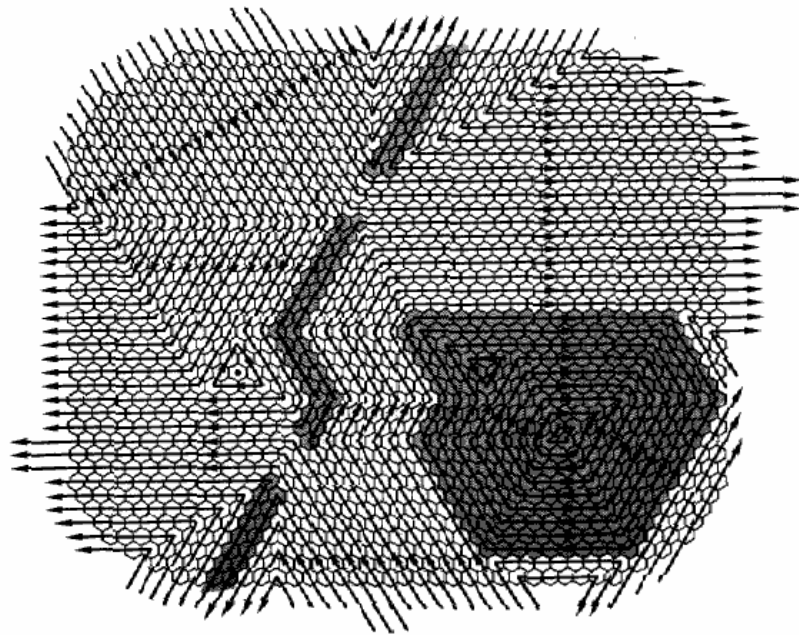


Figure © M.P. Allen and D.J. Tildesley 1987, from *Computer Simulation of Liquids*, Oxford U. Press p. 36

# 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

$$\mathcal{U} = \sum_i \mathcal{U}_1(\mathbf{r}_i) + \sum_i \sum_{j>i} \mathcal{U}_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_i \sum_{j>i} \sum_{k>j>i} \mathcal{U}_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$$

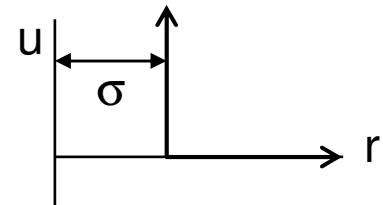
- \*  $\mathcal{U}_1$ : External field
- \*  $\mathcal{U}_2$ : Pairwise interactions (most important)
- \*  $\mathcal{U}_3$ : Three-body potentials (better, but costly)

# Common Pair Potentials

## \* Hard sphere

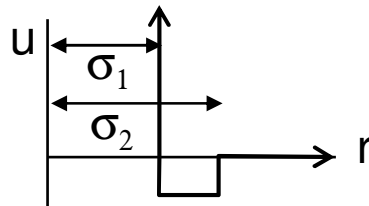
✓ Purely repulsive

$$u^{HS}(r) = \begin{cases} \infty & (r < \sigma) \\ 0 & (r \geq \sigma) \end{cases}$$



## \* Square well

✓ Idealized minimum

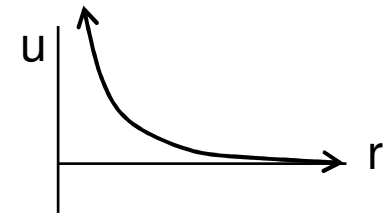


$$u^{SW}(r) = \begin{cases} \infty & (r < \sigma_1) \\ -\epsilon & (\sigma_2 \leq r < \sigma_1) \\ 0 & (r \geq \sigma_2) \end{cases}$$

## \* Soft sphere

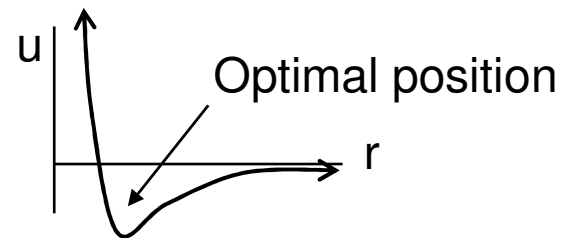
✓ Continuous, repulsive

$$u^{SS}(r) = ar^{-\nu}$$



## \* Lennard-Jones (most widely used)

$$u^{LJ}(r) = 4\epsilon \left[ \underbrace{\left(\frac{\sigma}{r}\right)^{12}}_{\text{repulsive}} - \underbrace{\left(\frac{\sigma}{r}\right)^6}_{\text{attractive}} \right]$$



# More Complex Pair Potentials

## \* Coulombic

- ✓ Ionic systems, unusually long-range

$$u^{zz}(r_{ij}) = \frac{z_i z_j}{4\pi\epsilon_0 r_{ij}}$$

Permittivity of free space

## \* Molecules

- ✓ United atoms for rigid units (e.g. CH<sub>2</sub>)
- ✓ 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)

