

# Statistical Mechanics: Ensembles, etc.

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# Thermodynamics:

Establishes relation between a small number of variables sufficient to describe the bulk behavior of a macroscopic system ( $N \sim 10^{23}$  particles)

A phenomenological theory of matter drawing concepts from experiments

## Thermodynamic variables:

Liquid, Gas  $\rightarrow$  P, V, T  
Magnetic Solid  $\rightarrow$  H, M, T

## Thermodynamic Potentials:

Internal Energy	Helmholtz Free Energy	Gibbs Free Energy	Enthalpy	Grand Potential
$U$	$A = U - TS$	$G = A + PV$	$H = U + PV$	$\Omega_G = U - TS - \sum_i N_i \mu_i$

# Maxwell Relations:

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}; \left(\frac{\partial V}{\partial N}\right)_{P,T} = \left(\frac{\partial \mu}{\partial P}\right)_{T,N}; \left(\frac{\partial S}{\partial N}\right)_{P,T} = -\left(\frac{\partial \mu}{\partial T}\right)_{P,N}$$

## Calculation of thermodynamic quantities:

$$C_V = \left(\frac{dQ}{dT}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V;$$

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T;$$

$$C_P = \left(\frac{dQ}{dT}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$$

$$K_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S, \text{ etc.}$$

$$C_P - C_V = T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \xrightarrow[\text{Maxwell Equations}]{\text{Use}} = -T \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2$$

$$\frac{C_P}{C_V} = \frac{K_T}{K_S}$$

# Thermodynamic Equilibrium:

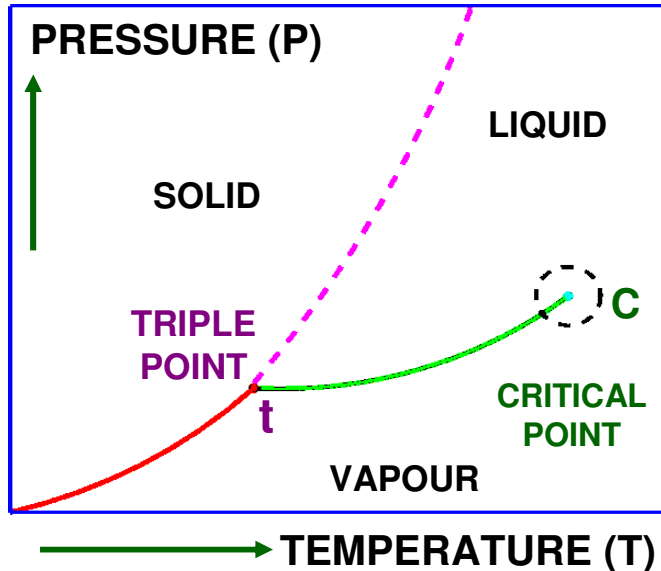
$N_1, V_1, E_1$	$N_2, V_2, E_2$
$T_1, P_1, \mu_1$	$T_2, P_2, \mu_2$

$$T_1 = T_2$$

$$P_1 = P_2$$

$$\mu_1 = \mu_2$$

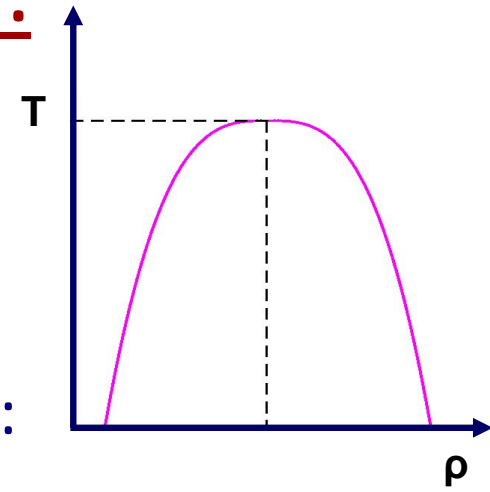
# Thermodynamics of Phase Transition:



$(P_t, T_t) \rightarrow$  Triple point  
 $(P_c, T_c) \rightarrow$  Critical point

Crossing Co-existence lines:  
 1<sup>st</sup> order phase transition

C  $\rightarrow$  2<sup>nd</sup> order phase transition



Magnetization

$$m \sim t^\beta$$

Specific Heat

$$C \sim t^{-\alpha}$$

Susceptibility

$$\chi \sim t^{-\gamma}$$

Correlation Length

$$\xi \sim t^{-\nu}$$

# Statistical Mechanics:

- Gets equilibrium properties of macroscopic systems from Microscopic considerations

- Microstate:

3N canonical coordinates  $q_1, q_2, \dots, q_{3N}$   
3N canonical momenta  $p_1, p_2, \dots, p_{3N}$  } **Phase Space**

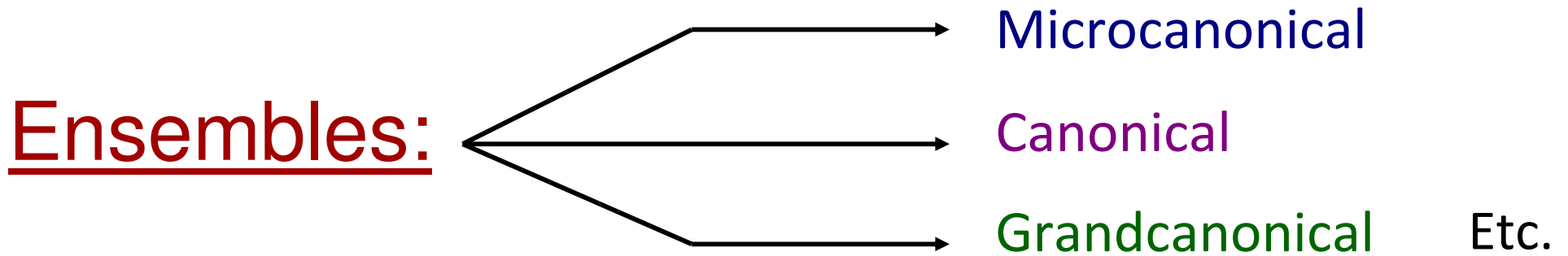
$$\dot{q} = \frac{\partial H(p, q)}{\partial p_i}; \quad \dot{p} = - \frac{\partial H(p, q)}{\partial q_i}$$

- Macrostate:

Isolated system:  $N, V, E$  constant      In reality never works!

$N, V, E + \Delta \rightarrow$  Infinite number of microstates satisfy it

Forms **ENSEMBLE**



$\rho(p, q, t)$ : Manner in which the members of the ensemble are distributed over all possible microstates at different instants of time

Stationary Ensemble:  $\frac{\partial \rho}{\partial t} = 0$  → System in equilibrium

Ensemble average  $\langle f \rangle$  independent of time

Liouville's Equation:  $\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0$

- Representative points in the phase space move in the same manner as an incompressible fluid

# Liouville's Equation Contd.

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0$$

➤ Equivalent to 6N Hamilton equations of motion of an N-particle system and is the most fundamental equation in Statistical Mechanics

$$\frac{\partial \rho}{\partial t} = 0$$

→ Only a requirement for equilibrium

$$\frac{d\rho}{dt} = 0$$

→ comes from the basic mechanics of particles and quite generally true

$[\rho, H] = 0 \rightarrow$  ensures simultaneous validity of  $\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} = 0$

$\rho(p, q)$  = constant over relevant region of phase space  
 = 0 elsewhere

→ “any member of the ensemble is equally likely to be in any one of the various possible microstates”

→ Postulates of

**EQUAL APRIORI PROBABILITIES**

Resulting Ensemble: Microcanonical

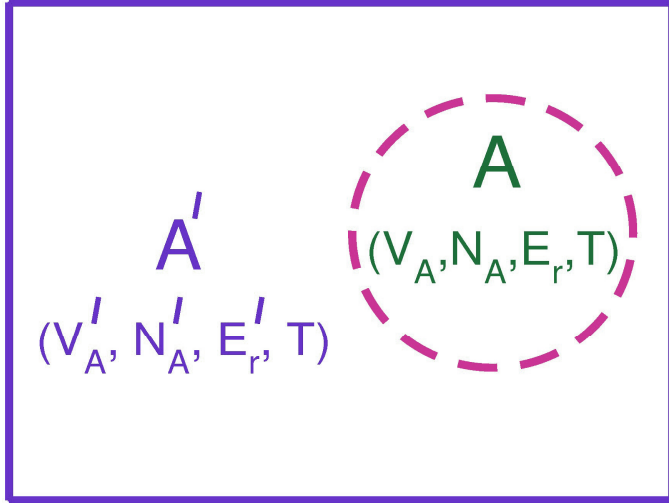
More general way of getting  $[\rho, H] = 0$  :

$$\rho(p, q) = \rho[H(p, q)]$$

Provides a class of density fluctuations for stationary ensemble



# Canonical Ensemble:



$$\rho(p, q) \propto \exp\left[-\frac{H(p, q)}{k_B T}\right]$$

System (smaller) of interest is in thermal equilibrium with a larger system (reservoir)

From now on:

$$P_r \propto \exp[-\beta E_i] = \frac{\exp[-\beta E_i]}{\sum_i \exp[-\beta E_i]}$$

# Partition function:

$$Z = \sum_i \exp[-\beta E_i]$$

$Z$  stands for Summe (sum over all states)

In most physical cases the energy levels accessible to a system are degenerate 10

$$Z = \sum_i g_i \exp[-\beta E_i]; \quad P = \frac{g_i \exp[-\beta E_i]}{Z}$$

In continuum situation  
(large system)

$$P(E)dE = \frac{\exp[-\beta E]g(E)dE}{Z} \quad Z = \int_0^{\infty} \exp[-\beta E]g(E)dE$$

## Thermodynamic Connections:

$$U = \bar{E} = \frac{\sum_i E_i \exp[-\beta E_i]}{\sum_i \exp[-\beta E_i]} = -\frac{\partial}{\partial \beta} \ln \left[ \sum_i \exp(-\beta E_i) \right]; \Rightarrow U = -\frac{\partial}{\partial \beta} \ln Z$$

$$U = \left[ \frac{\partial(\beta A)}{\partial \beta} \right]_{N,V} \Rightarrow -\frac{\partial}{\partial \beta} \ln Z = \left[ \frac{\partial(\beta A)}{\partial \beta} \right]_{N,V}$$
$$\Rightarrow \beta A = -\ln Z$$

$$A = -k_B T \ln Z$$

Once the potentials are known thermodynamic variables can be calculated

Thus  $Z$  is the important quantity in statistical ensemble

Microcanonical Ensemble	Canonical Ensemble
Energy Fluctuation restricted to a very narrow range	In principle, energy can be anywhere in the available range

**Question** : Thermodynamic properties of a system derived through different ensembles would be same?

**Answer** comes from the estimate of range over which the energy can actually extend over in Canonical case.

$$U = \langle E \rangle = \frac{\sum_i E_i \exp[-\beta E_i]}{\sum_i \exp[-\beta E_i]}$$

$$\frac{\partial U}{\partial \beta} = -\frac{\sum_i E_i^2 \exp[-\beta E_i]}{\sum_i \exp[-\beta E_i]} + \frac{\left[ \sum_i E_i^2 \exp[-\beta E_i] \right]^2}{\left[ \sum_i \exp[-\beta E_i] \right]^2} = \langle E \rangle^2 - \langle E^2 \rangle$$

$$\langle (\Delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = -\left( \frac{\partial U}{\partial \beta} \right) = k_B T^2 \left( \frac{\partial U}{\partial T} \right)$$

$$\langle (\Delta E)^2 \rangle = k_B T^2 C_V$$

Next: how energy is distributed among various members of the ensemble?

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$$P(E)dE \propto \exp(-\beta E) g(E) dE$$

Decreases with E

Increases with E

Product will have some extremum at some  $E^*$

actually a maximum  
Most probable value

$$\frac{\partial}{\partial E} \left\{ e^{-\beta E} g(E) \right\}_{E=E^*} = 0$$

$$\Rightarrow \left[ -\beta g(E) e^{-\beta E} + e^{-\beta E} \frac{\partial g(E)}{\partial E} \right]_{E=E^*} = 0; \Rightarrow \beta = \frac{\partial}{\partial E} \ln g(E) \Big|_{E=E^*}$$

We restrict ourselves around the mean value  $E = \langle E \rangle = U$

In microcanonical ensemble:

$$S = k_B \ln g$$

$$k_B \beta = \frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{E=U}$$

$\Rightarrow E^* = U = \langle E \rangle \rightarrow$  Most probable value  $\equiv$  mean value

Expand  $P(E)$  around  $E = E^* = \langle E \rangle = U$

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$$\ln \left[ e^{-\beta E} g(E) \right] = \left( -\beta U + \frac{S}{k_B} \right) + \frac{1}{2} \frac{\partial^2}{\partial E^2} \ln \left\{ e^{-\beta E} g(E) \right\}_{E=U} (E - U)^2 + \dots$$

$$= -\beta(U - TS) - \frac{1}{2k_B T^2 C_V} (E - U)^2 + \dots$$

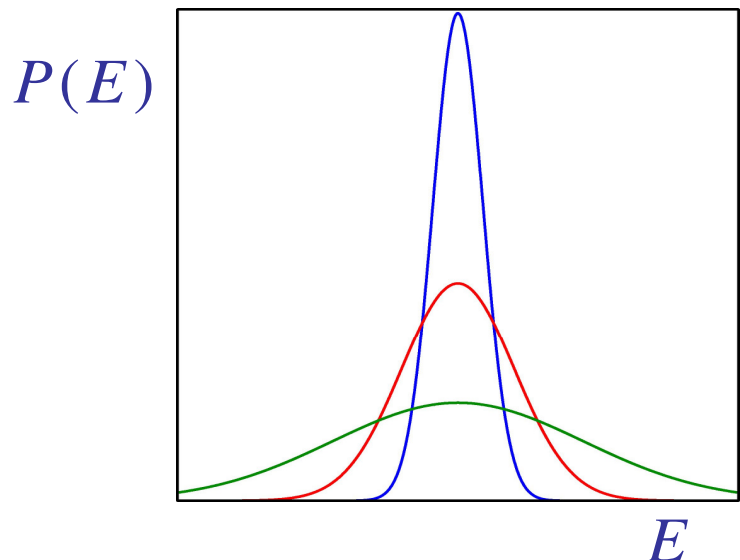
$$P(E) \propto e^{-\beta E} g(E) \simeq e^{-\beta(U-TS)} \exp \left\{ -\frac{(E-U)^2}{2k_B T^2 C_V} \right\}$$

Gaussian distribution with mean  $U$  and dispersion  $\sqrt{k_B T^2 C_V}$

Introduce reduced variable  $x = E / U$

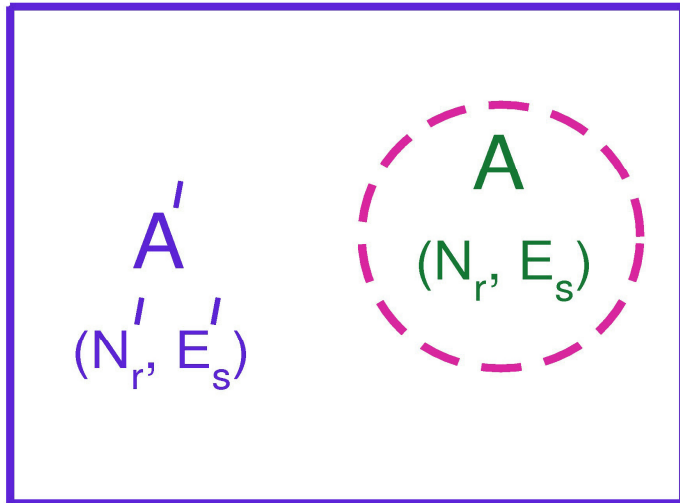
→ mean unity, dispersion  $\sqrt{k_B T^2 C_V} / U \sim O(N^{-1/2})$

$N \rightarrow \infty$  we have a delta function



Thus energy fluctuation will essentially be very restricted as in microcanonical ensemble

# Grandcanonical Ensemble:



Smaller system can exchange energy and particles with the reservoir

Grand canonical partition function:

$$\mathcal{Z} = \sum_{r,s} \exp[-\beta(E_s - \mu N_r)]$$

Define  $n = N / V$

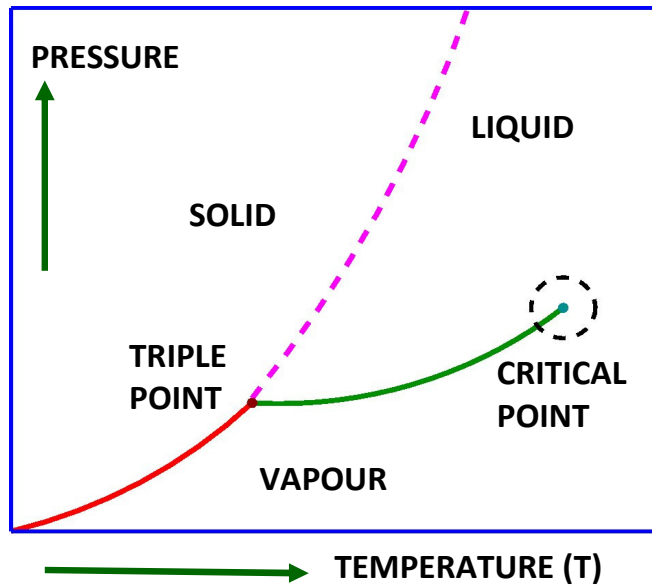
$$\frac{\overline{(\Delta n)^2}}{\bar{n}^2} = \frac{\overline{(\Delta N)^2}}{\bar{N}^2} = \frac{k_B T}{\bar{N}^2} \left( \frac{\partial \bar{N}}{\partial \mu} \right)_{T,V} = \frac{k_B T}{V} K_T$$

Small for  $V \rightarrow \infty$  if  $K_T$  is finite.

→ So equivalent to canonical ensemble



# Gas-Liquid Critical Point:



$$\rho_L - \rho_C \sim t^\beta, K_T \sim t^{-\gamma}, \text{ etc. ; } t = |T - T_C|$$

$$\overline{(\Delta n)^2} = \frac{k_B T}{V} K_T$$

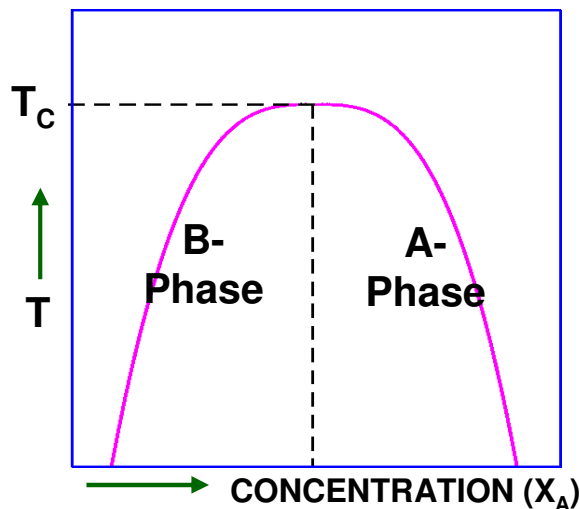
- ❖ In such a situation, results obtained from grandcanonical ensemble can lead to different results than in canonical ensemble
- ❖ In fact in such a situation **grandcanonical** is the appropriate ensemble

# Semigrandcanonical Ensemble:

Useful in multicomponent system, say a binary mixture (A+B)

Canonical in the sense that total number of particles is conserved, but particles can change identity ( $A \rightarrow B$  or  $B \rightarrow A$ )

Useful to study phase separation in a binary fluid or alloy.



Boltzmann factor:

$$\propto \exp \left[ -\beta (E - (\mu_A - \mu_B)) \right]$$

# Model

Symmetric Binary Lennard-Jones Mixture (A+B)

Density=1  $\rightarrow$  Incompressible

$$V(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$$

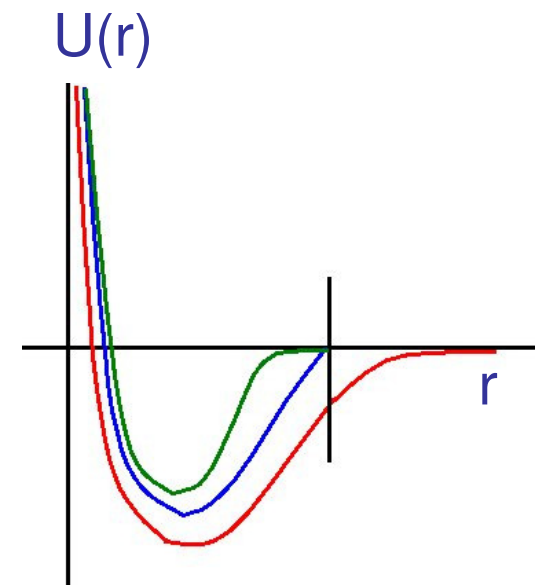
$$U(r_{ij}) = V(r_{ij}) - V(r_c) - (r_c - r_{ij}) \left. \frac{dV(r_{ij})}{dr_{ij}} \right|_{r_{ij}=r_c}$$

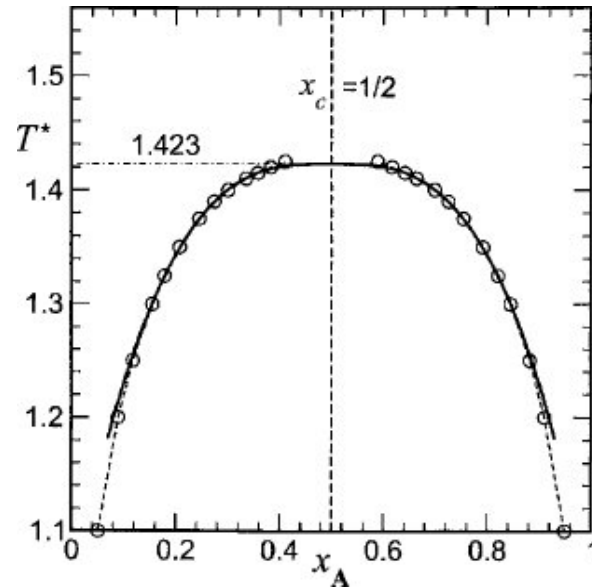
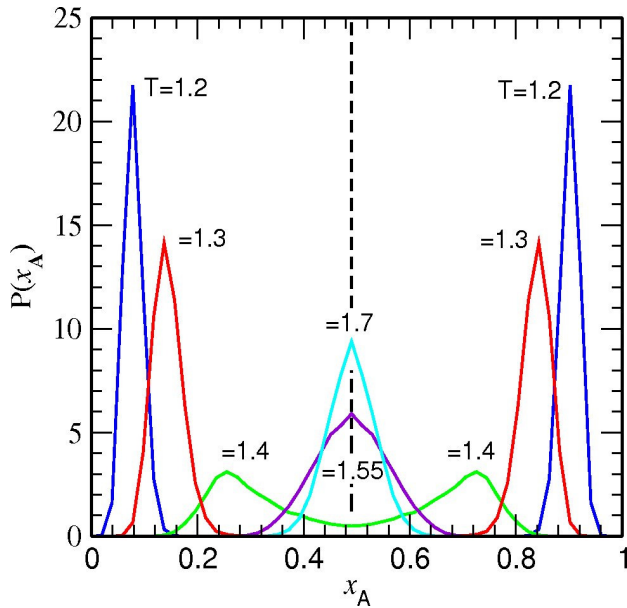
for  $r_{ij} \leq r_c$

$$= 0$$

for  $r_{ij} > r_c$

$$\epsilon_{AA} = \epsilon_{BB} = 2\epsilon_{AB} = \epsilon$$





$$m = B(T_c - T)^\beta$$

$$\beta = 0.325$$

Binary Fluid:

$$m = x_A - x_C ; x_C = 1/2$$

$$k_B T_C = 1.423 \varepsilon$$

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# Thank You