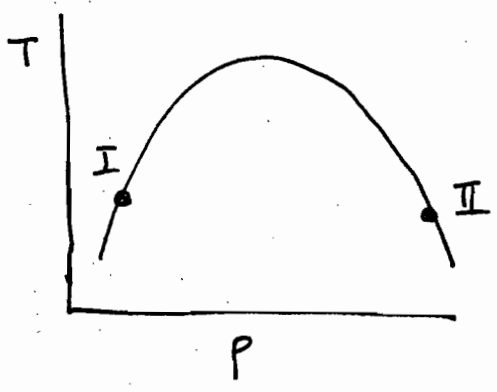# The Gibbs Ensemble

AZP, Molec. Phys. <u>81</u>, 506 (1987)

For calculations of phase equilibria in a one-component system:
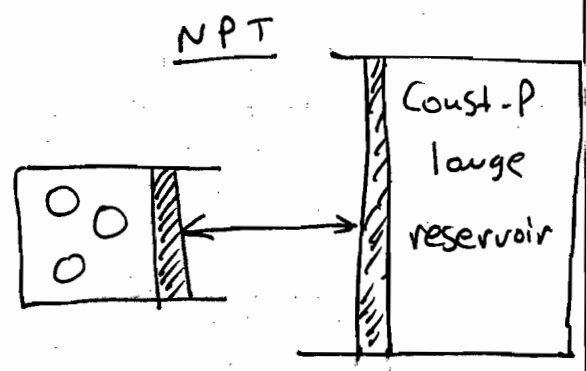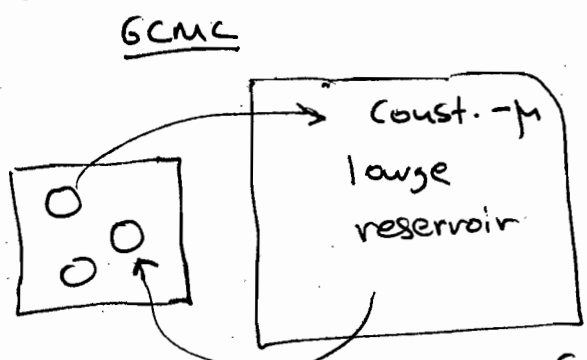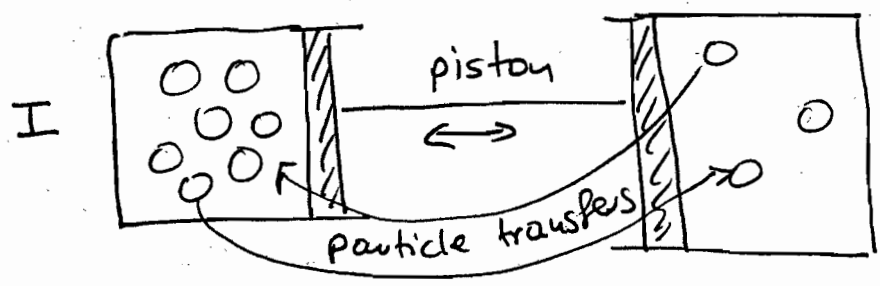

Equil. between phases I and II @ const. T
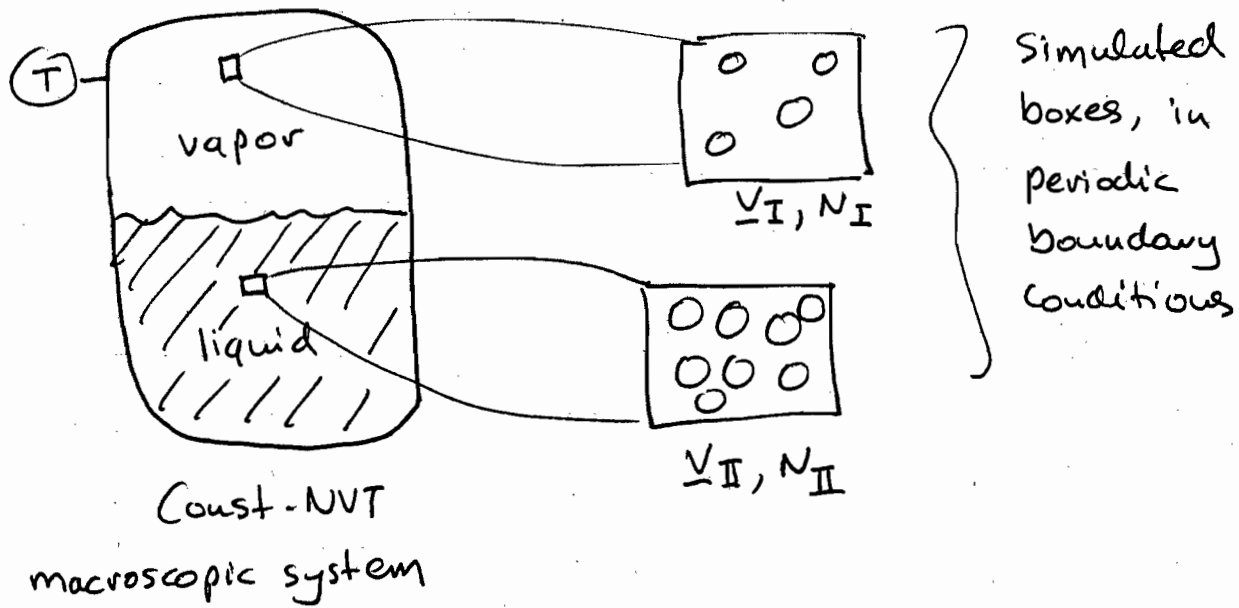
$$\mu^{I} = \mu^{II}$$
$$p^{I} = p^{II}$$

In NPT or μVT simulations, we set the pressure or chemical potential of a system by equilibrating it against an external reservoir:

The key idea of the Gibbs ensemble is to achieve equality of chemical potentials and pressures in the two regions of interest by <u>coupling</u> them:

Simulated boxes, in periodic boundary conditions

$\underline{V}_I, N_I$

$\underline{V}_{II}, N_{II}$

Const - NVT macroscopic system

Probability of a microstate with region I containing N_I particles in volume V_I, region II N_{II} particles in volume $V_{II} =$ (number of microstates of I) × (number of micro-states of II) × $\exp\left[-B(u_I + u_{II})\right]$

$$= \frac{1}{N_I!} \cdot V_I^{N_I} \cdot \frac{1}{N_{II}!} V_{II}^{N_{II}} \cdot \exp(-Bu_I - Bu_{II})$$

We need to perform three different types of moves to sample microstates properly:

Displacement moves

$$P_{displace} = \min\left[1, \exp(-B\Delta u_I - B\Delta u_{II})\right]$$

This is the same as normal NVT simulation in the two boxes. It is more efficient to perform displacement moves separately in each region.

Control acceptance of displacement moves by changing Δr_{max} to achieve acceptance of $\sim 30\% - 50\%$

Volume Changes

$$V_I \rightarrow V_I + \Delta V \qquad V_{II} \rightarrow V_{II} - \Delta V$$

$$P_{volume} = \min\left[1, \left(\frac{V_I + \Delta V}{V_I}\right)^{N_I} \cdot \left(\frac{V_{II} - \Delta V}{V_{II}}\right)^{N_{II}} \cdot \exp(-\beta(\Delta U_I + \Delta U_{II}))\right]$$

In many cases, one of the two regions has a much smaller density than the other (e.g. vapor at equilibrium with liquid). Since we want a "reasonable" number of particles in both phases, we must have $V_{vapor} \gg V_{liquid}$, so acceptance of volume changes is controlled by the liquid.

Particle Transfers

$$N_{II} \rightarrow N_{II} - 1 \qquad N_I \rightarrow N_I + 1 \qquad \text{for transfer of}$$
a particle from region II to region I.

$$P_{transfer} = \min\left[1, \exp\left(-\beta \Delta U_I - \beta \Delta U_{II}\right) \times \frac{N_{II}}{V_{II}} \times \frac{V_I}{N_I + 1}\right]$$

Particle transfer steps can have very low acceptance probabilities for dense phases, which limits the practical applicability of the Gibbs ensemble method in its original form.
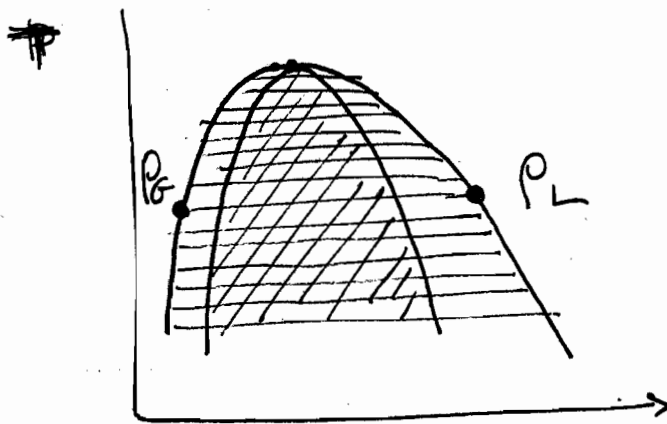
Ratios of moves

To satisfy detailed balance, the move type must be decided at random with fixed probabilities. Typical

ratios are

displacement : volume change : transfer = 100 : 1 : 200

The ratio of attempted transfers to overall moves is determined by the need to have a "reasonable" number of successful transfers (>1,000) over a simulation run.

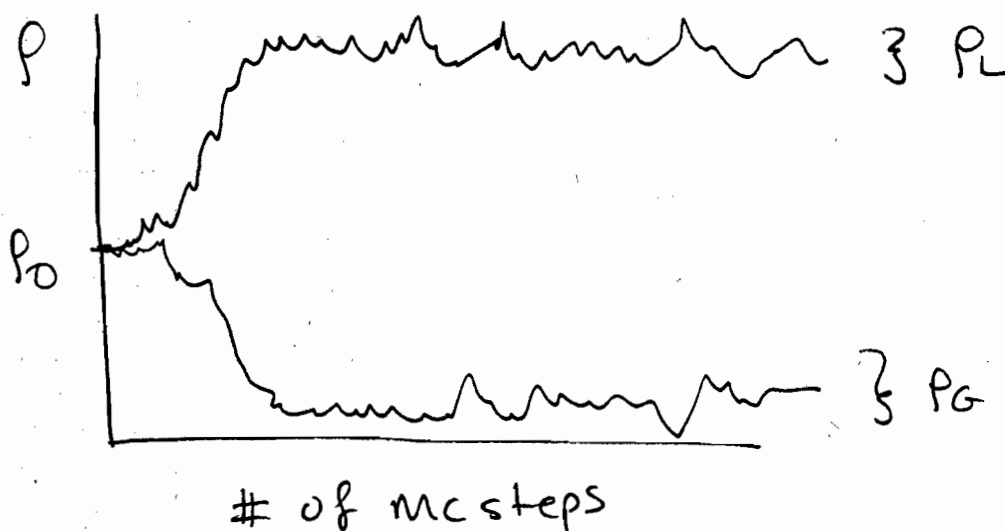### Starting Condition


≡ 2-phase region

╫╫ unstable region (inside spinodal)

A system with initial density in the unstable region quickly phase separates to reduce its overall free energy - same as in lab experiment:

# of mc steps

Mixtures

The method can be applied in the same form to multicomponent mixtures. The particle transfer step applies to each component separately.

For mixtures, there are additional degrees of freedom that allow simulations at constant-P:
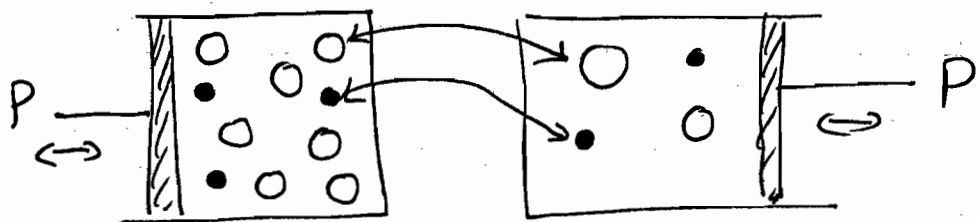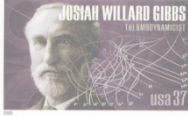

transfers of
both components

For const-P Gibbs ensemble simulations,

$$P_{volume} = \min\left[1, \left(\frac{V_I + \Delta V_I}{V_I}\right)^{N_I} \times \left(\frac{V_{II} + \Delta V_{II}}{V_{II}}\right)^{N_{II}} \cdot \exp\left[-\beta \Delta U - P(\Delta V_I + \Delta V_{II})\right]\right.$$

(for pure components, the vapor pressure is not a degree of freedom at constant T)

Origins and Development
of the Gibbs Ensemble Methodology
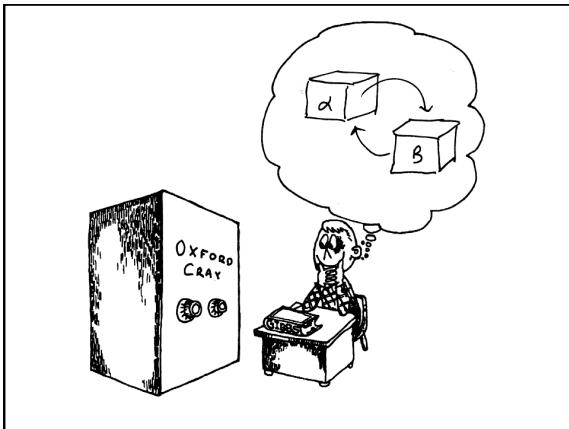
Athanassios Z. Panagiotopoulos

**Direct determination of phase coexistence properties of fluids by
Monte Carlo simulation in a new ensemble**

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A methodology is presented for Monte Carlo simulation of fluids in a new ensemble that can be used to obtain phase coexistence properties of multicomponent systems from a single computer experiment. The method is based on performing a simulation simultaneously in two distinct physical regions of generally different densities and compositions. Three types of perturbations are performed, a random displacement of molecules that ensures equilibrium within each region, an equal and opposite change in the volume of the two regions that results in equality of pressures, and random transfers of molecules that equalize the chemical potentials of each component in the two regions. The method is applied to the calculation of the liquid–gas coexistence envelope for the pure Lennard-Jones (6, 12) fluid for several reduced temperatures from the vicinity of the triple point to close to the critical point ($T^* = 0.75$ to $T^* = 1.30$). Good overall agreement with previously available literature results is obtained, with some deviations at the extremes of this temperature range.

$$P_{acc} = e^{-\beta\Delta U} \times \quad 1 \quad \left(\frac{V_I - \Delta V}{V_I}\right)^{N_I} \left(\frac{V_{II} + \Delta V}{V_{II}}\right)^{N_{II}} \quad \frac{N_I V_{II}}{(N_{II}+1)V_I}$$

Pure LJ fluid, $T^* = kT/\varepsilon = 1.10$, $N_{tot} = 300$

Reduced Density $\rho^* = \rho\sigma^3$ vs CPU time (s) on Intel Xeon @ 3 GHz

citations / year

total = 1407
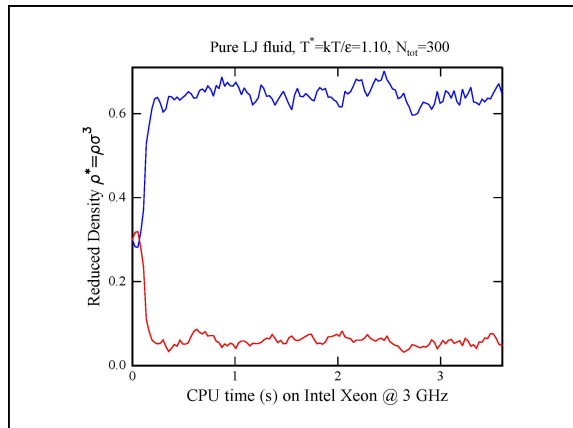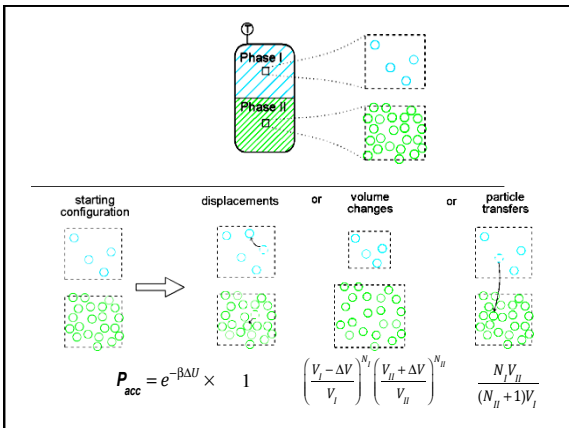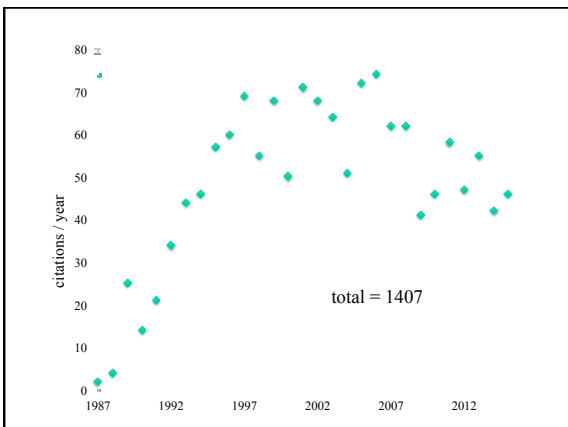
Configurational bias – continuous space

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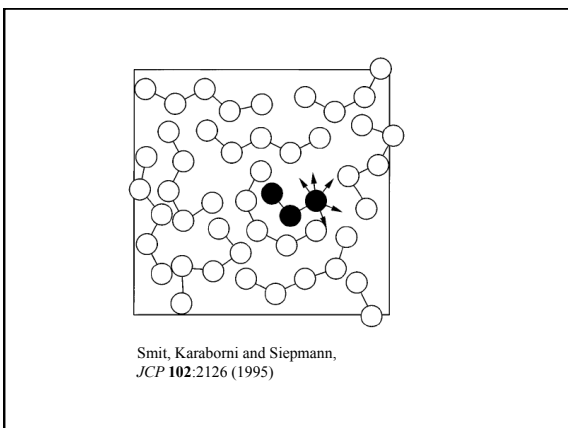
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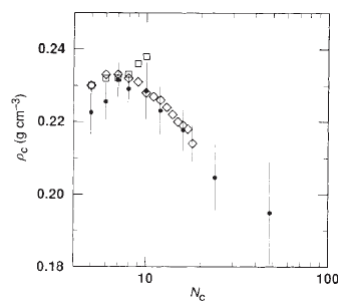
Transferable Potentials for Phase Equilibria. 7. Primary, Secondary, and Tertiary Amines, Nitroalkanes and Nitrobenzene, Nitriles, Amides, Pyridine, and Pyrimidine

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TABLE 1: Nonbonded TraPPE Parameters for Nitrogen-Containing Molecules

functional group	model	pseudoatom	σ (Å)	ϵ/k_B (K)	q (e)
alkyl tail	UA	CH$_3$	3.75	98	0
	UA	CH$_2$	3.95	46	0
	EH	C(methyl)	3.3	4	0
	EH	C(methylene)	3.65	5	0
	EH	H(alkyl)	3.31	15.3	0
arene	UA	CH(aro, not α)	3.74	48	0
amine	EH	C$^\alpha$(amine)	σ(C$_{alkyl}$)	ϵ(C$_{alkyl}$)	+0.18
	EH	N(1° amine)	3.34	111	−0.892
	EH	N(2° amine)	3.52	58	−0.745
	EH	N(3° amine)	3.78	12	−0.54
	EH	H(1° amine)	0	0	+0.356
	EH	H(2° amine)	0	0	+0.385
nitro	UA	C$^\alpha$(aro, nitro)	4.50	15	+0.14
	EH	C$^\alpha$(nitro)	σ(C$_{alkyl}$)	ϵ(C$_{alkyl}$)	+0.14
	UA/EH	N(nitro)	3.31	40	+0.82
	UA/EH	O(nitro)	2.90	80	−0.48
nitrile	UA	CH$_3^\beta$(nitrile)	σ(CH$_3$)	ϵ(CH$_3$)	+0.269
	UA	C(sp, nitrile)	3.55	60	+0.129
	EH	C$^\beta$(nitrile)	σ(C$_{alkyl}$)	ϵ(C$_{alkyl}$)	+0.269
	EH	C(sp, nitrile)	3.48	67.5	+0.129
	UA/EH	N(nitrile)	2.95	60	−0.398
amide	EH	N(1° amide)	3.34	111	−0.8
	EH	H(1° amide)	0	0	+0.4
	EH	C(carbonyl)	3.72	34	+0.424
	EH	O(carbonyl)	3.05	79	−0.424
N(aro)	UA	N−(CH)−CH	3.74	48	+0.33
	UA	N−(CH)−N	3.90	47	+0.66
	UA	CH−(N)−CH	3.45	28	−0.66

From dimer to condensed phases at extreme conditions: Accurate predictions of the properties of water by a Gaussian charge polarizable model

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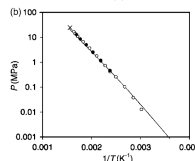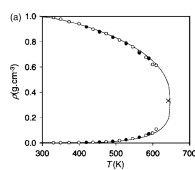
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FIG. 3. Vapor-liquid coexistence of water: (a) saturated densities; (b) vapor pressures. Coexistence points of the GCPM model are obtained with GEMC simulations of N=300 and N=512 molecules and compared with experimental data (solid lines)

FIG. 5. Site-site pair correlation functions of the water model determined with *NPT* Monte Carlo simulations, at ambient , *T*=298 K, *P*=0.1013 MPa and high temperature , *T*=573 K, *P*=10 MPa conditions, are compared with the neutron diffraction data of Soper (2000) solid lines. The high temperature data are shifted for a comparison on the same graph.

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