

Compressibility and fluctuations

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Grandcanonical partition function in semiclassical approximation:

$$-k_B T \ln Z_{\mu VT} = F - \mu(N) = \Omega = -pV, \text{ where } Z_{\mu VT} = \sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{N! \Lambda^{3N}} \int e^{-\beta E} d\vec{r}_1 \dots d\vec{r}_N$$

System of N identical particles in the grandcanonical ensemble (μVT), μ = parameter

$$\langle N \rangle = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{V,T} = \frac{\sum_{N=0}^{\infty} N \frac{e^{\beta \mu N}}{\Lambda^{3N} N!} \int e^{-\beta E} d\vec{r}_1 \dots d\vec{r}_N}{\sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{\Lambda^{3N} N!} \int e^{-\beta E} d\vec{r}_1 \dots d\vec{r}_N} = \frac{\sum_{N=0}^{\infty} N \frac{e^{\beta \mu N}}{\Lambda^{3N} N!} Q_N}{\sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{\Lambda^{3N} N!} Q_N}$$

$$\left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T} = \beta \frac{\sum_{N=0}^{\infty} N^2 \frac{e^{\beta \mu N}}{\Lambda^{3N} N!} Q_N \times \sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{\Lambda^{3N} N!} Q_N - \left(\sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{\Lambda^{3N} N!} Q_N \right)^2}{\left(\sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{\Lambda^{3N} N!} Q_N \right)^2} = \beta \text{Var } N$$

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$$\left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T} = \beta \text{Var } N$$

Grandcanonical potential: $\Omega = F - \mu N = -pV = -\beta^{-1} \ln Z_{\mu VT}$

$$dF = -SdT - pdV + \mu dN$$

Differential: $d\Omega = -pdV - Vdp = -SdT - pdV - Nd\mu \Rightarrow Nd\mu = Vdp$ [T, N, V]

Another derivation: $dG = Nd\mu = Vdp$ [T, N]

ρ and μ are intensive variables, hence they depend on $\rho = \langle N \rangle / V$ only:

$$N \left(\frac{\partial \mu}{\partial N} \right)_{T,V} = V \left(\frac{\partial \rho}{\partial N} \right)_{T,V} = \left(\frac{\partial \rho}{\partial (N/V)} \right)_T = \frac{1}{N} \left(\frac{\partial \rho}{\partial (1/V)} \right)_{T,N} = \frac{V}{N} \left[-V \left(\frac{\partial \rho}{\partial V} \right)_{T,N} \right] = \frac{1}{\rho \kappa_T}$$

Eventually:

$$\frac{\text{Var } N}{\langle N \rangle} = \rho k_B T \kappa_T$$

isothermal compressibility:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N}$$

bulk modulus:

$$B_T = 1/\kappa_T$$

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$$\frac{\text{Var } N}{\langle N \rangle} = \rho k_B T \kappa_T$$

• larger compressibility \Rightarrow larger fluctuations

• $\text{Var } N > 0 \Rightarrow \kappa_T > 0$ ($\kappa_T < 0$ for a mechanically unstable system)

• $\text{Var } \rho = \frac{\rho^3 k_B T \kappa_T}{N} \xrightarrow{N \rightarrow \infty} 0$ (thermodynamic limit)

typical "finite-size effect" is $\mathcal{O}(1/N)$

Exceptions:

• diffusivity in MD: $\mathcal{O}(1/N^{1/3})$ – a particle interacts with its periodic image $\propto 1/N^{1/3}$ apart

• crystals: $\mathcal{O}(\log N/N)$ – counting phonons

• plasma, ionic solutions (more terms): $\mathcal{O}(1/N^{3/2})$ – Debye-Hückel

• some 2D systems: $\mathcal{O}(\log N/N)$

• critical point – critical exponents

RDF in the μVT ensemble and compressibility

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$$\rho^2 g(r) = \frac{\sum_{N=2}^{\infty} N(N-1) \frac{e^{\beta \mu N}}{N! \Lambda^{3N}} \int \exp(-\beta U) d\vec{r}_3 \dots d\vec{r}_N}{\sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{N! \Lambda^{3N}} \int \exp(-\beta U) d\vec{r}_1 \dots d\vec{r}_N}, \quad r = |\vec{r}_1 - \vec{r}_2|$$

$$\Rightarrow \text{Compressibility equation } 1 + \rho \int [g(r) - 1] d\vec{r} = \frac{\text{Var } N}{\langle N \rangle} = \rho k_B T \kappa_T$$

spherical symmetry: $\int d\vec{r} = \int_0^{\infty} 4\pi r^2 dr$

• More fluctuation and correlation quantities can be expressed by similar integrals (Kirkwood-Buff)

• Numerically ill-defined for large r – must be cut off

• Tricks to be able to use the NVT ensemble

Exercise 1. Show that $g_{\mu VT}(r) = 1$ for monoatomic ideal gas

Hint: for ideal gas $e^{\beta \mu N} / \Lambda^3 = p / k_B T = \langle N \rangle / V = \rho$

Exercise 2. Calculate κ_T from the compressibility equation with the canonical RDF ($N = \text{constant}$)

undirrektionale Kompressibilität $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N}$

Simulation in other ensembles

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• NVE \rightarrow NVT (MD), measuring: $T \rightarrow E$

• NVT \rightarrow NVE (MC), measuring: $E \rightarrow T$

• NVT \rightarrow NPT (MC, MD), measuring: $P \rightarrow V$

• NVT \rightarrow μVT (MC, [MD]), measuring: $\mu \rightarrow N$

In the thermodynamic limit ($N \rightarrow \infty$) equivalent, otherwise errors $\propto 1/N^*$

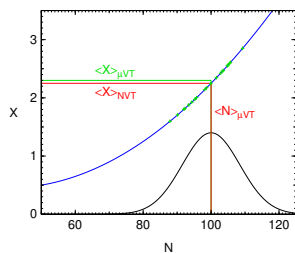
Corrections:

$$\langle X \rangle_{\mu VT} - \langle X \rangle_{NVT} \approx \frac{1}{2} \left(\langle (N - \langle N \rangle)_{\mu VT}^2 \rangle_{\mu VT} \left(\frac{\partial^2 \langle X \rangle_{\mu VT}}{\partial N^2} \right)_{V,T} \right) = \frac{k_B T}{2N} \left(\frac{\partial \rho}{\partial p} \right)_T \rho^2 \left(\frac{\partial^2 \langle X \rangle}{\partial \rho^2} \right)_T$$

where $\langle \cdot \rangle$ in the last derivative is either $\langle \cdot \rangle_{\mu VT}$ or $\langle \cdot \rangle_{NPT}$

Derivation: Taylor expansion of $X(N)$ okolo $\langle N \rangle$

The corrections become important near the critical point



* not for: nonperiodic b.c., (surface $N^{2/3}$), crystals ($\ln N/N$), diffusivity ($N^{1/3}$)...

MC in the microcanonical ensemble

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MC move under constraint $E = \text{const}$ = problem

It is possible in the classical mechanics for $E_{\text{pot}} + E_{\text{kin}} = \text{const}$: can be integrated over momenta (not so trivial, though).

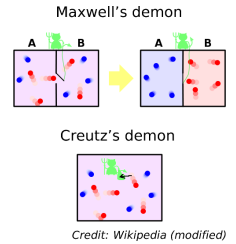
Approximate solution – Creutz

$$E = E_{\text{max}} \rightarrow E \leq E_{\text{max}}$$

(do not buy a melon in a many-dimensional space)

Creutz demon has a bag with energy: $E_{\text{bag}} = E_{\text{max}} - E \geq 0$

E_{bag} has the Boltzmann distribution \Rightarrow temperature



Credit: Wikipedia (modified)

Creutz – Metropolis comparison

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• Choose a particle (lattice site, ...) to move

• $A^{\text{tr}} := A^{(k)} + \text{random move of the chosen particle}$

• $\Delta U := U(A^{\text{tr}}) - U(A^{(k)}) \equiv U^{\text{tr}} - U^{(k)}$

• The configuration is accepted ($A^{(k+1)} := A^{\text{tr}}$) with probability $\min\{1, e^{-\beta \Delta U}\}$ otherwise rejected:

Metropolis	Creutz	Creutz–Metropolis
$u := u(0,1)$		$\text{bag} = -k_B T \ln u(0,1)$
IF $u < e^{-\beta \Delta U}$	IF $\Delta U < \text{bag}$	IF $\Delta U < \text{bag}$
THEN $A^{(k+1)} := A^{\text{tr}}$	THEN $A^{(k+1)} := A^{\text{tr}}$; $\text{bag} -= \Delta U$	THEN $A^{(k+1)} := A^{\text{tr}}$; $\text{bag} -= \Delta U$
ELSE $A^{(k+1)} := A^{(k)}$	ELSE $A^{(k+1)} := A^{(k)}$	ELSE $A^{(k+1)} := A^{(k)}$

in all cases (bag) = $k_B T$ (in continuous world: $-\ln u(0,1) = 1$)

• $k := k + 1$ and again and again

NPT ensemble in MC

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To incorporate volume change, (X) must be in the form of an \int of probability density: $\vec{r}_i = V^{1/3} \xi_i$

$$\langle X \rangle = \frac{1}{Q_{\text{NPT}}} \int_0^{\infty} \int_{V_N} X(\vec{r}^N, V) \frac{1}{V} \exp\{-\beta[pV + U(\vec{r}^N)]\} d\vec{r}^N dV$$

$$= \frac{1}{Q_{\text{NPT}}} \int_0^{\infty} \int_{1^{3N}} X(V^{1/3} \xi^N, V) \frac{1}{V} V^N \exp\{-\beta[pV + U(V^{1/3} \xi^N)]\} d\xi^N dV$$

Microreversible volume change: $V^{\text{tr}} = V + u_{(-d,d)}$, then

$$p_{\text{acc}} = \min\{1, (V^{\text{tr}}/V)^{N-1} \exp[-\beta p(V^{\text{tr}} - V)] \exp[-\beta(U^{\text{tr}} - U)]\}$$

$N/V, -1$: exact ideal gas βp , const: $\mathcal{O}(1/N)$ error

Better option: $V^{\text{tr}} = V \exp[u_{(-d,d)}]$ ($\ln V$ is uniformly sampled), then:

$$p_{\text{acc}} = \min\{1, (V^{\text{tr}}/V)^{N+1-1} \exp[-\beta p(V^{\text{tr}} - V)] \exp[-\beta(U^{\text{tr}} - U)]\}$$

• Usually N one-particle moves (translations:rotations = 1:1) per one volume-change move

• Acceptance ration of volume changes ~ 0.3

• General problem: global change of configuration \Rightarrow slow convergence \Rightarrow not good for too large systems

Grandcanonical ensemble in MC

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• MC step: change the number of particles by ± 1

$$\vec{r}_i = V^{1/3} \xi_i$$

$$\langle X \rangle = \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{\Lambda^{3N} N!} \int X(\vec{r}^N, N) \exp[-\beta U_N(\vec{r}^N)] d\vec{r}^N$$

$d\vec{r}^N$ depends on $N \rightarrow$ dimensionless coordinates $\vec{r}_i = V^{1/3} \xi_i$

$$\langle X \rangle = \frac{1}{\Xi} \sum_{N=0}^{\infty} \int_{1^{3N}} X(V^{1/3} \xi^N, N) \frac{e^{\beta \mu N V}}{\Lambda^{3N} N!} \exp[-\beta U_N(V^{1/3} \xi^N)] d\xi^N$$

• Insert or remove a particle with the same probability 1/2

$$P_{\text{insert particle}} = \min\left\{1, \frac{e^{\beta \mu V}}{\Lambda^3 (N+1)} \exp\{-\beta[U_{N+1}(\vec{r}^{N+1, \text{zkus}}) - U_N(\vec{r}^N)]\}\right\}$$

$$P_{\text{remove particle}} = \min\left\{1, \frac{N \Lambda^3}{e^{\beta \mu V}} \exp\{-\beta[U_{N-1}(\vec{r}^{N-1, \text{zkus}}) - U_N(\vec{r}^N)]\}\right\}$$

Problem: insert a large molecule

Solution: gradually

$$e^{\beta \mu} = \Lambda^3 e^{\beta \mu_{\text{res}}} (N/V)$$

Grandcanonical ensemble in MD

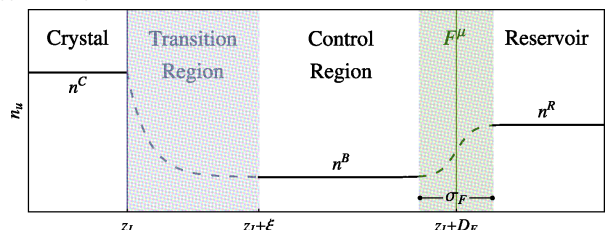
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• The same as in MD, but "continuously" – problematic

• C μ MD [Perego, Salvalaglio, Parrinello, DOI: 10.1063/1.4917200]

• Reservoir with molecules, region with a force \Rightarrow change of the (chem.) pot.

• Applied to crystallization with a constant oversaturation of the solution



Reaction ensemble in MC

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- We can easily calculate a chemical equilibrium in an ideal gas phase.
But what if the mixture is not ideal? 1) Calculate μ_i, γ_i, \dots 2) Reaction ensemble

Reaction (reactants: $v_i < 0$, products: $v_i > 0$): $\sum_{i=1}^k v_i A_i = 0$

Equilibrium: $\Delta_r G_m = \sum_{i=1}^k v_i \mu_i = 0$

Generalized partition function of a mixture, $N = \sum_{i=1}^k N_i$ (constant N_i):

$$Z(N_1, \dots, N_k, V, T) = \prod_{i=1}^k \frac{(q_i/\Lambda_i^3)^{N_i}}{N_i!} \times \int \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^N$$

Balance (extent of reaction = ζ): $N_i = N_i^{(0)} + \zeta v_i$

$$Z(N_1^{(0)}, \dots, N_k^{(0)}, V, T) = \sum_{\zeta} \prod_{i=1}^k \frac{(V q_i / \Lambda_i^3)^{N_i^{(0)} + \zeta v_i}}{(N_i^{(0)} + \zeta v_i)!} \times \int \exp[-\beta U(V^{1/3} \xi^N)] d\xi^N$$

Reaction ensemble in MC

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Reaction "move" $\zeta^{\text{tr}} = \zeta + \Delta\zeta$ accepted with probability

$$p_{\text{acc}} = \min \left\{ 1, K'^{\Delta\zeta} \exp(-\beta\Delta U) \prod_{i=1}^k \frac{(N_i^{(0)} + \zeta v_i)!}{(N_i^{(0)} + \zeta^{\text{tr}} v_i)!} \right\}$$

where

$$\Delta U = U(V^{1/3} \xi^N, \zeta^{\text{tr}}) - U(V^{1/3} \xi^N, \zeta)$$

$$\tilde{v} = \sum_{i=1}^k v_i$$

$$K' = \prod_{i=1}^k \left(\frac{V q_i}{\Lambda_i^3} \right)^{v_i} = \left(\frac{V p}{kT} \right)^{\tilde{v}} \exp \left(-\frac{\sum \mu_{i,\text{id}}}{kT} \right) = \left(\frac{V p}{kT} \right)^{\tilde{v}} K$$

where $\Delta_r G_m^{\circ} = N_A \sum \mu_{i,\text{id}}$ is the reaction molar Gibbs energy (for $p =$ standard pressure) and K is the equilibrium constant (for the standard state ideal gas at pressure p).

Reaction step

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- Random change of the extent of the reaction: with probability $1/2$ " \rightarrow " ($\zeta^{\text{tr}} = \zeta + 1$) with probability $1/2$ " \leftarrow " ($\zeta^{\text{tr}} = \zeta - 1$)
- Random selection of the corresponding number of reactant and product molecules
- Replacement of reactants \rightarrow products (for $\Delta\zeta = \zeta^{\text{tr}} - \zeta > 0$) or products \rightarrow reactants (for $\Delta\zeta < 0$)
- Calculate the energy change ΔU
- New configuration accepted with probability p_{acc}

Note: Some degrees of freedom are simulated, some not...

Nonspherical molecules:

$$\exp \left[\frac{-\mu_{i,\text{id}}}{kT} \right] = \frac{q_i k_B T}{q_i^{\text{model}} p_{\text{st}}^{\text{tr}}} \quad q_i^{\text{model}} = \int \exp(-\beta U_{\text{int}}) d(\text{intern. deg. of freedom})$$

Eg., general hard molecule: $q_i^{\text{model}} = 8\pi^2 \Rightarrow K'$ must be divided by product $\prod_{i=1}^k (q_i^{\text{model}})^{v_i}$

- Again, gradual insertion may be needed
- Final result = equilibrium composition

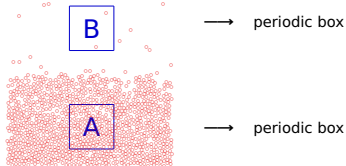
Gibbs ensemble

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Determine vapor-liquid (fluid-fluid) phase equilibrium:

- 1) MD: slab geometry, bad for low T (water + BuOH, 373 K) \rightarrow
- 2) MC, MD: μ in the liquid, μ gas from the virial EoS
- 3) Gibbs ensemble [A. Panagiotopoulos (1987)]

One-component system:



- $T = \text{const}$, $V = V_A + V_B = \text{const}$, $N = N_A + N_B = \text{const}$
 \Rightarrow to be satisfied: $p_A = p_B$ and $\mu_A = \mu_B$
- Gibbs phase law: 1 degree of freedom \Rightarrow pressure is determined

Gibbs ensemble: one-component system

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$$Q_{\text{NVT}} = \sum_{N_A=0}^N \int_0^V dV_A V_A^{N_A} \int d\xi_A^N e^{-\beta U_A(N_A)} \frac{V_B^{N_B}}{N_B!} \int d\xi_B^N e^{-\beta U_B(N_B)}$$

- Volume change $V_A^{\text{tr}} = V_A + \Delta V$ a $V_B^{\text{tr}} = V_B - \Delta V$, acceptance probability:

$$p_{\text{acc}} = \min \left\{ 1, \exp \left[-\beta \Delta U_A - \beta \Delta U_B + N_A \ln \frac{V_A + \Delta V}{V_A} + N_B \ln \frac{V_B - \Delta V}{V_B} \right] \right\}$$

- Particle transfer from box B to box A, acceptance probability:

$$p_{\text{acc}} = \min \left\{ 1, \exp \left[-\beta \Delta U_A - \beta \Delta U_B - \ln \frac{(N_A + 1)V_B}{N_B V_A} \right] \right\}$$

- Particle transfer from box A to box B, acceptance probability:

$$p_{\text{acc}} = \min \left\{ 1, \exp \left[-\beta \Delta U_B - \beta \Delta U_A - \ln \frac{(N_B + 1)V_A}{N_A V_B} \right] \right\}$$

- Standard MC moves – translations, rotations.

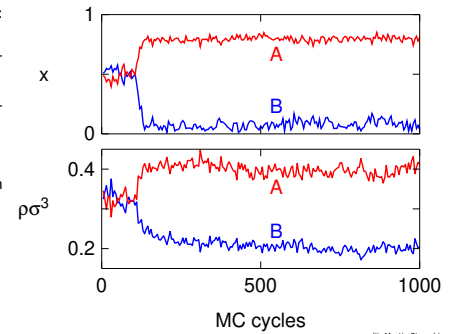
Usually 1 volume change + 1-several article transfers per N single-particle moves.

Gibbs ensemble: mixture

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Gibbs phase law for a binary mixture:
2 degrees of freedom
 $T = \text{const}$, $p = \text{const}$, equilibrium compositions are determined

- Volume changes in both boxes separately (see NPPT)
- Particle transfer
- Useful: particle exchange between boxes – higher probability



credit: Martin Strad1

Exercise – Madelung constant of NaCl

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For the electrostatic energy of a crystal it holds (per 1 molecule of NaCl)

$$E_{\text{el}} = \frac{M a^2}{4\pi\epsilon_0 a}$$

where $a =$ lattice constant and $M =$ Madelung constant

- Simulate a NaCl crystal while decreasing temperature to zero.
Use data:
 $T=0$ tau, $T=0.2$
cutoff=8 LJcutoff=cutoff
tau, $P=0.2$ bulkmodulus=1e11 ;
! restart after cooling
el.epsk=0.1 el.epsr=0.1 el.grid=1024 ! higher precision
init="start" no=1;
- Determine the box size and calculate a
- Determine the electrostatic energy and express it per 1 NaCl
- Calculate the Madelung constant

–1.74756