PHY 341/641
Thermodynamics and Statistical Physics

Lecture 16

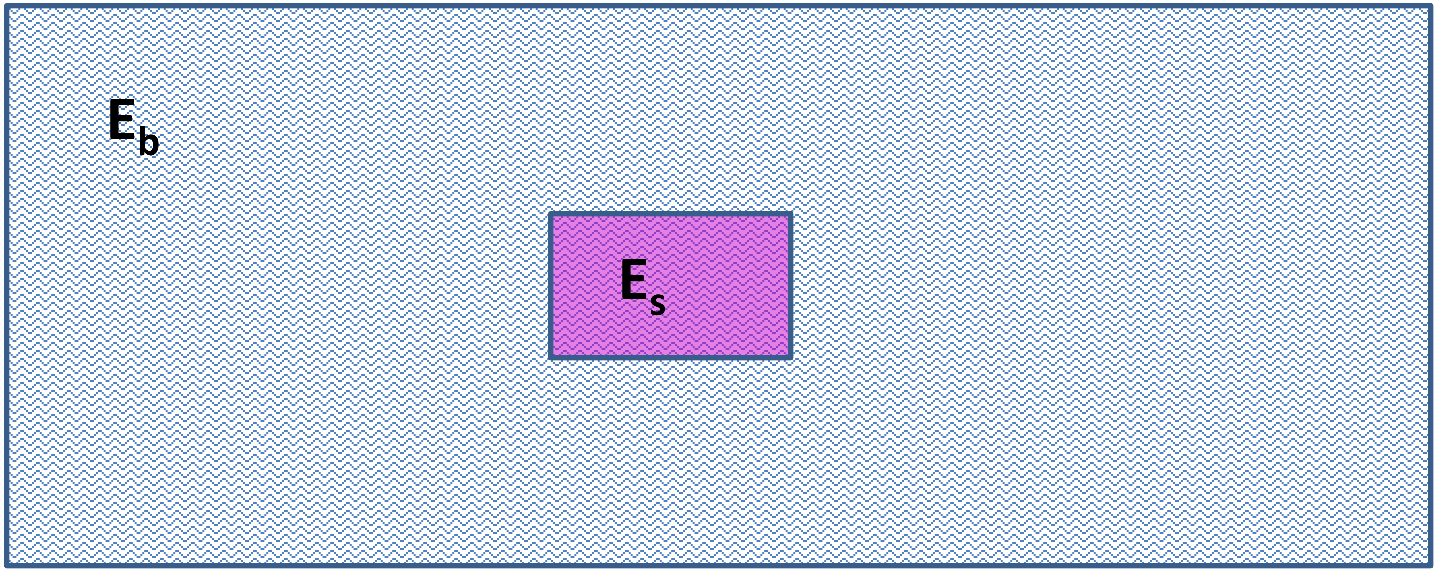
Methodologies of statistical mechanics. (Chapter 5 in STP)

A. Simulations of ensembles
B. Examples of ensembles for spin systems

5	1/27/2012	Entropy	2.15-2.19	HW 5	1/30/2012
6	1/30/2012	Thermodynamic Potentials	2.20-2.21	HW 6	2/1/2012
7	2/01/2012	Thermodynamic Potentials	2.22-2.24	HW 7	2/3/2012
8	2/03/2012	Introduction to probability theory	3.1-3.3	HW 8	2/6/2012
9	2/06/2012	Probability distributions	3.4-3.5	HW 9	2/8/2012
10	2/08/2012	Continuous distributions/Central limit theorem	3.6-3.10	HW 10	2/10/2012
11	2/10/2012	Introduction to statistical mechanics	4.1-4.2	HW 11	2/13/2012
12	2/13/2012	Enumeration of microstates	4.3	HW 12	2/15/2012
13	2/15/2012	Many particle systems	4.4-4.5	HW 13	2/17/2012
14	2/17/2012	Microcanonical ensemble	4.6	HW 14	2/20/2012
15	2/20/2012	Canonical ensemble	4.7-4.8	HW 15	2/22/2012
16	2/22/2012	Grand canonical ensemble	4.9-4.12	HW 16	2/24/2012
17	2/24/2012	Review			
	2/27/2012	APS -- no class; take-home exam			
	2/29/2012	APS -- no class; take-home exam			
	3/02/2012	APS -- no class; take-home exam			
	3/05/2012				

Review:

Canonical ensemble:



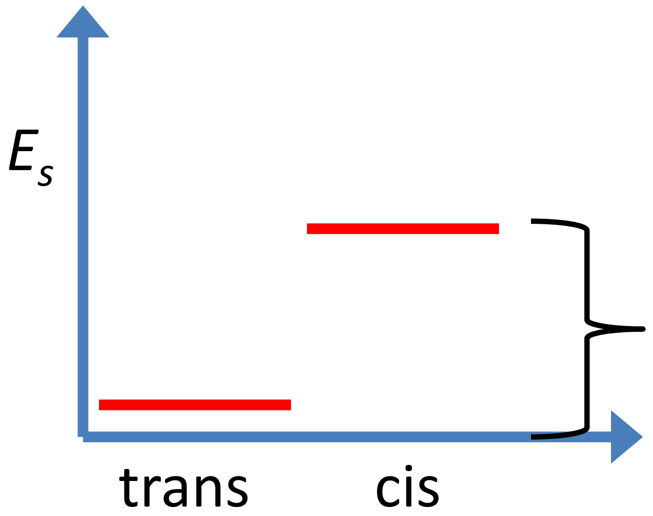
Partition function :

$$Z \equiv \sum_{s'} e^{-E_{s'}/kT} \equiv \sum_{s'} e^{-\beta E_{s'}} = Z(T,V,N)$$

Probability of state s :

$$\mathcal{P}_s = \frac{1}{Z} e^{-E_s/kT}$$

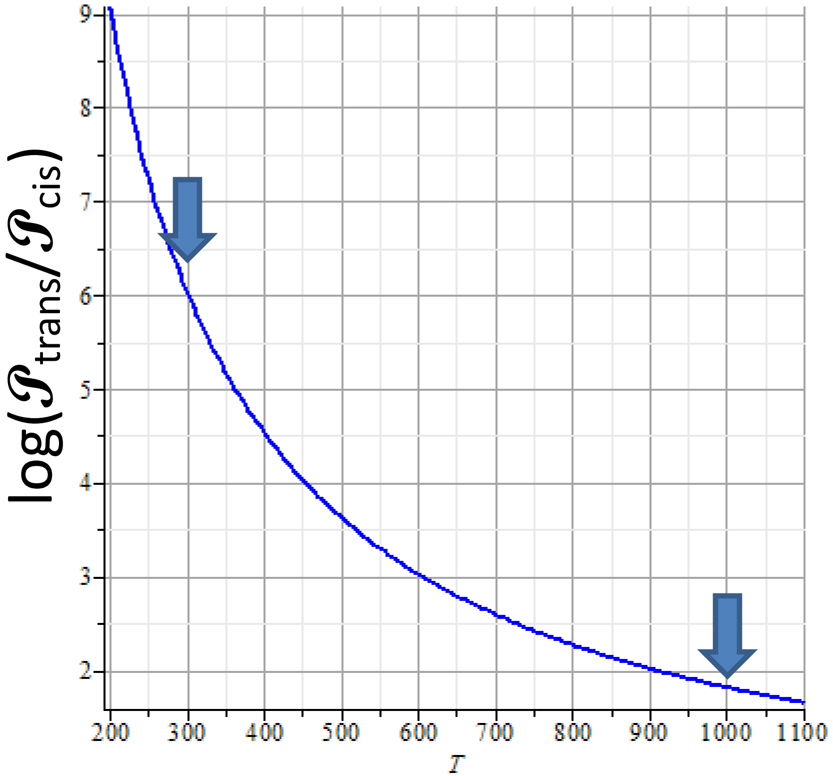
Example of canonical ensemble (Prob. 4.24 in STP)



$$\Delta E / k = 4180K$$

$$\frac{\mathcal{P}_{trans}}{\mathcal{P}_{cis}} = \frac{e^{-E_{trans}/kT}}{e^{-E_{cis}/kT}} = e^{-(E_{trans}-E_{cis})/kT}$$

$$\frac{\mathcal{P}_{trans}}{\mathcal{P}_{cis}} = e^{4180/T}$$



Simulation of the canonical ensemble

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 21, NUMBER 6 JUNE, 1953

Equation of State Calculations by Fast Computing Machines

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(Received March 6, 1953)

A general method, suitable for fast computing machines, for investigating such properties as equations of state for substances consisting of interacting individual molecules is described. The method consists of a modified Monte Carlo integration over configuration space. Results for the two-dimensional rigid-sphere system have been obtained on the Los Alamos MANIAC and are presented here. These results are compared to the free volume equation of state and to a four-term virial coefficient expansion.

I. INTRODUCTION

THE purpose of this paper is to describe a general method, suitable for fast electronic computing machines, of calculating the properties of any substance

II. THE GENERAL METHOD FOR AN ARBITRARY POTENTIAL BETWEEN THE PARTICLES

In order to reduce the problem to a feasible size for numerical work, we can, of course, consider only a finite

[Link to pdf file of article]

Consider calculating the average energy of a canonical ensemble at temperature T based on averaging M samples.

$$\langle E \rangle = \frac{\sum_{s=1}^{M} E_s e^{-E_s/kT}}{\sum_{s=1}^{M} e^{-E_s/kT}}$$

Metropolis algorithm:

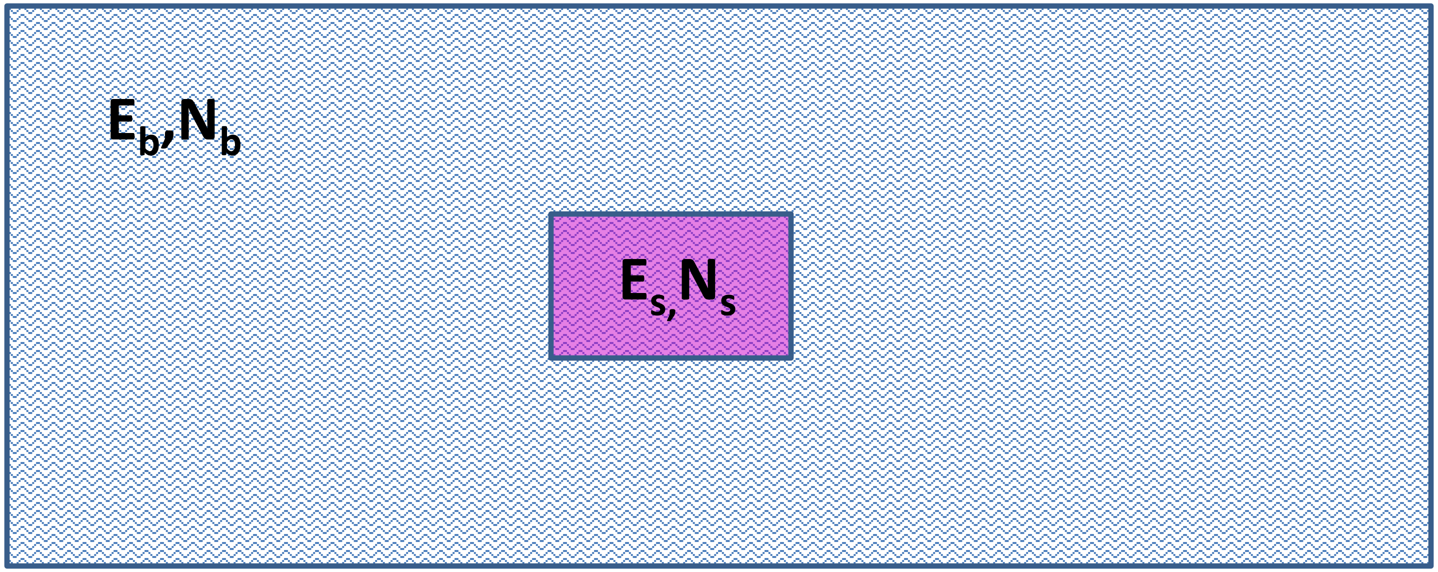
1. Start the simulation with a random choice of microstates to compose a system state *s*.
2. Choose a random microstate *a* to *b* and calculate the change of the system energy from ε_b-ε_a:

$$\frac{\mathcal{P}_b}{\mathcal{P}_a} = \frac{e^{-\varepsilon_b/kT}}{e^{-\varepsilon_a/kT}} = e^{-(\varepsilon_b - \varepsilon_a)/kT}$$

3. Examine $\Delta\varepsilon = \varepsilon_b - \varepsilon_a$:
    a. If $\Delta\varepsilon<0$ ➔ then accept the change.
    b. If $\Delta\varepsilon>0$ ➔ then accept the change with the probability $e^{-\Delta\varepsilon/kT}$. This can be done by generating a uniformly distributed random number r such that 0 < r < 1. If $r \leq e^{-\Delta\varepsilon/kT}$ then accept the new state otherwise, retain the previous state.
4. Repeat steps 2 and 3 M times, accumulating the summations in the numerator and denominator.
5. Compute the average.

Note: Some of the programs at the www.compadre.org/stp site use this method.

Grand canonical ensemble



Assume $E_s \ll E_b$, $N_s \ll N_b$

$$\Rightarrow \mathcal{P}_s = C' e^{-(E_s - \mu N_s)/kT} \equiv C' e^{-\beta(E_s - \mu N_s)} \equiv \frac{1}{Z_G} e^{-\beta(E_s - \mu N_s)}$$

$$\text{where:} \qquad Z_G \equiv \sum_{s'} e^{-\beta(E_{s'} - \mu N_{s'})}$$

Summary of ensemble results:

	Partition function	Thermodynamic potential
Microcanonical	$\Omega(E,V,N)$	$S(E,V,N)=k\ln(\Omega)$
Canonical	$Z(T,V,N)$	$F(T,V,N)=-kT\ln(Z)$ $F=E-TS$
Grand canonical	$Z_G(T,V,\mu)$	$\Omega_{Landau}(T,V,\mu)=-kT\ln(Z_G)$ $\Omega_{landau}=F-\mu N$

Examples of ensembles for magnetic interactions (Chapter 5 in STP)

Microstates :

$$\varepsilon_i = -\mu s_i B \quad \text{where } s_i = \pm 1, \ \mu B \equiv \text{ spin alignment energy}$$

$$\mu \equiv \tfrac{1}{2} g \mu_B = -9.28 \times 10^{-24} \, J/T$$

$$Z_N = \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \sum_{s_3=\pm 1} \cdots \sum_{s_N=\pm 1} e^{\beta \mu B \left(\sum_{i=1}^{N} s_i \right)}$$

$$= \left(\sum_{s_1=\pm 1} e^{\beta \mu B s_1} \right)^N = \left(Z_1 \right)^N$$

Calculation of Z_1

$$Z_1 = \sum_{s_1=\pm 1} e^{\beta\mu B s_1} = e^{-\beta\mu B} + e^{\beta\mu B} = 2\cosh(\beta\mu B)$$

Thermodynamic functions:

$$F = -kT\ln\left(Z_1\right)^N = -NkT\ln Z_1 = -NkT\ln\left(2\cosh(\beta\mu B)\right)$$

$$\left\langle E \right\rangle = -N\frac{\partial \ln Z_1}{\partial \beta} = -N\mu B\tanh\left(\beta\mu B\right)$$

$$C = \left(\frac{\partial\left\langle E \right\rangle}{\partial T}\right)_B = kN\left(\beta\mu B\right)^2\operatorname{sech}^2\left(\beta\mu B\right)$$

Magnetic field dependence of Z:

$$Z_N(T,N,B) = \left(2\cosh(\beta\mu B)\right)^N$$

Magnetization :

$$M = \mu \sum_{i=1}^{N} \langle s_i \rangle$$

$$\langle s_i \rangle = \frac{\sum_{s_1=\pm 1} s_1 e^{\beta\mu B s_1}}{\sum_{s_1=\pm 1} e^{\beta\mu B s_1}} = \frac{1}{\beta\mu}\frac{\partial \ln Z_1}{\partial B}$$

$$\Rightarrow M = N\mu \tanh\left(\beta\mu B\right) = -\frac{\partial F}{\partial B}$$

$$\chi \equiv \left(\frac{\partial M}{\partial B}\right)_T = -\left(\frac{\partial^2 F}{\partial B^2}\right)_T = N\mu^2\beta\,\mathrm{sech}^2\left(\beta\mu B\right)$$