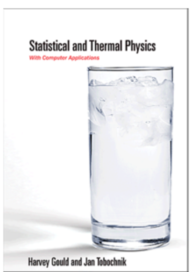
PHY 341/641
Thermodynamics and Statistical Physics

Lecture 2

1. Continued discussion of microscopic models (Chapter 1)
   a. Notion of equilibrium in statistical mechanics/thermodynamics
   b. Macrostates/microstates
2. Introduction to thermodynamics (Chapter 2)
   a. Definition of "the system"
   b. Thermodynamic variables (T, P, V, N, …)
   c. First law of thermodynamics

Review from last time --
Chapter 1 – From Microscopic to Macrosopic Behavior

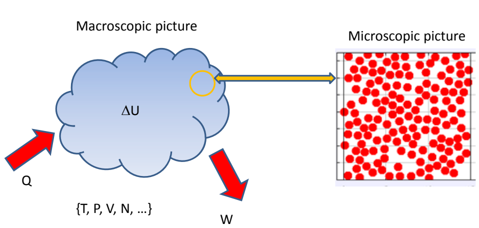


Assignment: Read Chapter 1 (quickly) during this week and checkout some of the corresponding simulations (HW 1 and HW 2) due Monday 1/23.

"The purpose of this introductory [material] is to whet your appetite… " The chapter introduces a lot of the concepts that we will use (more carefully) throughout the course.

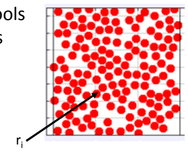
What will you learn?

Energy Analysis



Comment on simulation tools
Molecular dynamics

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i$$



$$\mathbf{F}_i = -\nabla_i \sum_{j \neq i} u_{pair}(|\mathbf{r}_i - \mathbf{r}_j|)$$

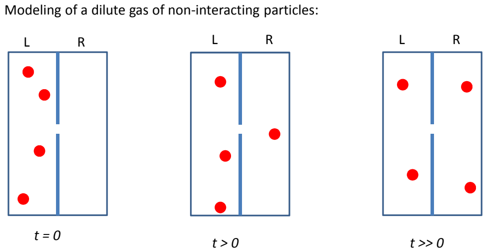
Example model pair potential (Lennard-Jones):

$$u_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

For an “ideal gas”--

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i \equiv 0$$

Modeling of a dilute gas of non-interacting particles:



$$P_{L\to R} = \frac{n}{N} \qquad P_{R\to L} = \frac{N-n}{N}$$

Enumeration of possibilities for N=4

Microstates	n	$P_{L \to R}$
L L L L	4	1/16
L L L R		
L L R L	3	4/16
L R L L		
R L L L		
L L R R		
L R R L		
R R L L	2	6/16
L R L R		
R L R L		
R L L R		
R R R L		
R R L R	1	4/16
R L R R		
L R R R		
R R R R	0	1/16

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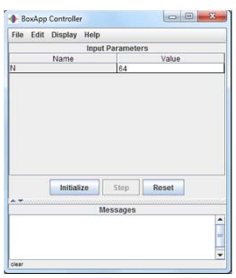
Simulation available from: http://www.compadre.org/STP/ stp_ApproachToEquilibrium.jar

Note: in order to easily control the simulation, you need to use:
Display → Switch GUI



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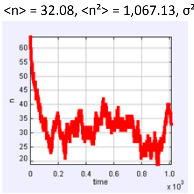
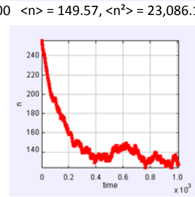
N=64, t≈1000 $\langle n\rangle = 32.08$, $\langle n^2\rangle = 1{,}067.13$, $\sigma^2 = 38.12$, $\sigma/\langle n\rangle = 0.19$



N=256, t≈1000 $\langle n\rangle = 149.57$, $\langle n^2\rangle = 23{,}086.17$, $\sigma^2 = 714.56$, $\sigma/\langle n\rangle = 0.18$



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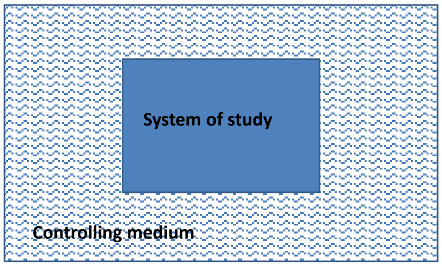
Macroscopic viewpoint – thermodynamics

(start reading Chapter 2)



Variables of thermodynamics

- **Temperature**
  - *T*
  - *Zeroth law of thermodynamics: Two systems in thermal equilibrium with a third system are in thermal equilibrium with eachother.*
- **Pressure**
  - *P=F/A*
- **Volume**
  - *V*
- **Number of particles**
  - *N*

The relationships between these variables depends on the "equation of state" of the system.

Examples of "Equations of State"

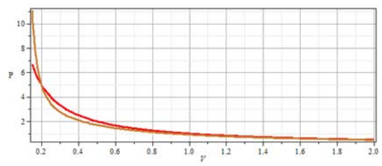
Ideal gas equation of state:

$$PV = Nk_BT \qquad k_B = 1.38\times10^{-23}\,\text{J/K}$$

van der Waals equation of state:

$$\left(P + \frac{N^2}{V^2}a\right)(V - Nb) = Nk_BT$$

Comparison of
- Ideal gas equation
- van der Waals gas equation



In general the "state" of a system will depend on the thermodynamic variables. For example, the internal energy:

$$U = U(N, T, P, V)$$

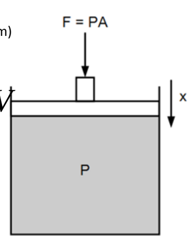
Thermodynamic "processes" ➔ change the state of the system

$$U_1(N_1, T_1, P_1, V_1) \Rightarrow U_2(N_2, T_2, P_2, V_2)$$

Thermodynamic process -- work (performed ON the system)

$$dW = -Fdx = -PAdx = -PdV$$

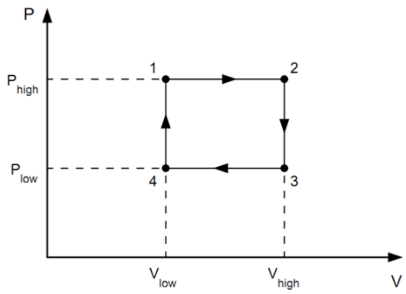
$$W_{1\to 2} = -\int_{V_1}^{V_2} P(T,V)dV$$



For an ideal gas at constant T :

$$W_{1\to 2} = -\int_{V_1}^{V_2} P(T,V)dV = -\int_{V_1}^{V_2} \frac{NkT}{V}dV = -NkT \ln \frac{V_2}{V_1}$$

Work performed during a cyclic process:



$$W_{net} = -\left(P_{high} - P_{low}\right)\left(V_{high} - V_{low}\right)$$

Thermodynamic process -- heat (added TO the system)

Q

For heat added TO the system: $Q > 0$

For heat withdrawn FROM the system: $Q < 0$

First law of thermodynamics

$$U_2 - U_1 \equiv \Delta U = W + Q$$

Example: Adiabatic expansion V_1 → V_2 for an ideal gas system

$$U_2 - U_1 \equiv \Delta U = W + Q = W$$

$$PV = NkT$$

To be continued…..