Energy and Multiplicity.
Optimization methods.

Friday, September 1, 2016
BME/CHE/PHY 558, Physical & Quantitative Biology
Rutgers University: Chemical Thermodynamics
Lecturer: Gábor Balázsi
Equilibrium points as extrema

[Diagram showing a curve with two points labeled as stable and unstable.]
Max-multiplicity gives the most likely outcome

Five molecules in a dividing cell:

Which configuration(s) will have the highest multiplicity?

What will be the highest multiplicity?

What will be its probability?

E.g., if all molecules in cell #1:

$$W(5,0) = \frac{5!}{5!0!} = 1$$

<table>
<thead>
<tr>
<th>Cell 1</th>
<th>Cell 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>12345</td>
<td>12345</td>
</tr>
</tbody>
</table>
Max-multiplicity gives the most likely outcome

Which configuration(s) will have the highest multiplicity?

What will be the highest multiplicity? 

\[ W(3, 2) = \frac{5!}{3!2!} = 10 \]

What will be its probability? 

\[ P(3, 2) = p^3(1 - p)^2 \frac{5!}{3!2!} = \left(\frac{1}{2}\right)^5 10 = 0.3125 \]
Effect of max-multiplicity is stronger at high $N$

Maxima given by:

$$\left. \frac{dW}{dn} \right|_{n^*} = 0$$

$$n^* = \frac{n}{2}$$

As a force increasing with $N$...
But there is no mechanical force at all.
Degrees of freedom and constraints

• Degrees of freedom are parameters that the system can change.

• Constraints are restrictions imposed on the system’s freedom.
Basic Problem of Thermodynamics

Goal: determine the equilibrium state that eventually results after the removal of internal constraints in a closed, composite system.
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\[ U^{(F)}, V^{(F)}, N_1^{(F)}, N_2^{(F)}, \ldots, N_M^{(F)} \]
Why do gases exert pressure?

Imagine 3 spheres that could occupy 3, 4 or 5 cells. Which case has highest multiplicity $W$?

Degree of freedom: Volume = number of spatial cells.

$W(A) = \frac{5!}{2!3!} = 10$  
$W(B) = \frac{4!}{3!1!} = 4$  
$W(C) = \frac{3!}{0!3!} = 1$

Spheres tend to occupy the largest possible volume (at constant temperature).

<table>
<thead>
<tr>
<th>Case</th>
<th>Configuration</th>
<th>Volume</th>
<th>$W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image1.png" alt="Configuration A" /></td>
<td>5 cells</td>
<td>10</td>
</tr>
<tr>
<td>B</td>
<td><img src="image2.png" alt="Configuration B" /></td>
<td>4 cells</td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td><img src="image3.png" alt="Configuration C" /></td>
<td>3 cells</td>
<td>1</td>
</tr>
</tbody>
</table>
Why do materials diffuse?

Imagine a permeable wall that separates 2 containers with black and white spheres. Degree of freedom: number of same-colored spheres on either side.

Particles tend to mix according to their relative fractions (here, 0.5 of each) on both sides.

<table>
<thead>
<tr>
<th>Case</th>
<th>Left</th>
<th>Right</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>![Diagram A]</td>
<td>( W(A) = \frac{4! \times 4!}{2! \times 2! \times 2! \times 2!} = 36 )</td>
</tr>
<tr>
<td>B</td>
<td>![Diagram B]</td>
<td>( W(B) = \frac{4! \times 4!}{3! \times 1! \times 1! \times 3!} = 16 )</td>
</tr>
<tr>
<td>C</td>
<td>![Diagram C]</td>
<td>( W(C) = \frac{4! \times 4!}{4! \times 0! \times 0! \times 4!} = 1 )</td>
</tr>
</tbody>
</table>

Permeable Barrier →
Why is rubber elastic?

Imagine a polymer chain with the left end fixed.

DoF: distance of the other end from the wall.

Multiplicity predicts that rubber tends to be neither completely extended nor completely flattened.
Work, energy, and heat
Definitions

**Work** is the effect of force, or it arises from energy conversion.

**Energy** is the capacity of a system to do work. It is always conserved.

- **Kinetic energy:** $K = \frac{mv^2}{2}$, where $m$ is mass, $v$ is velocity. Capacity to do work by movement.

- **Potential energy:** Capacity to do work based on position.

- **Internal energy:** Total energy of all particles + interactions in a system

**Heat** is a form of energy transfer specific to thermodynamics. It alters the internal energy of a system.
Forces and work

Assume a spring attached to the wall with spring constant $k_s$ and equilibrium position $x_1=0$. What is the work to extend the spring very slowly from position $x_1=0$ to position $x_2$?

Force exerted by spring:

$$f_s = -k_s (x - x_1)$$

Applied force opposes the spring’s force:

$$f_{ap} = -f_s = k_s (x - x_1)$$

Work done by applied force:

$$w = \int_{x_1}^{x_2} f_{ap} \, dx = \frac{k_s}{2} x_2^2$$

= potential energy
First Law of Thermodynamics

**First law:** Energy is conserved. Change in energy ($\Delta U$) = heat ($q$) + work ($w$).

\[ \Delta U = q + w \]

- $\Delta U$ : change of system’s internal energy
- $q$ : heat flowing into the system
- $w$ : work done on the system
First Law: a financial analogy

\[ \Delta U = q - w \]

- **\( \Delta U \):** change in account balance
- **\( q \):** interest (+); banking fees (-)
- **\( w \):** salary (+), withdrawals (-)
First Law: a human analogy

\[ \Delta U = q - w \]

\( \Delta U \): change of weight

\( q \) : food intake (calories); heat dispersed

\( w \) : work done by the system, exercise

World map of diet
Second Law of Thermodynamics

Systems change spontaneously to maximize the multiplicity of their microstates.

\[ W = \max \]
Second Law: Why do materials absorb heat?

Assume we have 3 particles and energy levels \( \varepsilon = 0, 1, 2, 3 \ldots \)
How many ways exist to achieve internal energy \( U = 0, 1, 2, 3 \) ?

Systems tend to increase their internal energy.
If you give them heat, they take it.
Second Law: Why and where does heat flow?

Assume 2 systems with energy levels $\epsilon=0, 1...$ and internal energies $U_A=2, U_B=4$.

\[
W_A = \frac{10!}{2!8!} = 45 \quad W_B = \frac{10!}{4!6!} = 210 \quad W_{total} = W_A W_B = 9450
\]

What happens if we set these systems in contact?

If $U_A=3, U_B=3$: $W_{total} = W_A W_B = \left(\frac{10!}{3!7!}\right)^2 = 14,400$ Heat flows from warm to cold.
Finding maxima and minima
Reminder: extrema of univariate functions

Continuous, smooth functions have minima or maxima where their derivative = 0.

Example: $f(x) = (x - 2)^2 \quad \frac{df}{dx} = 2(x - 2) = 0 \quad x^* = 2$

$\frac{d^2 f}{dx^2} = 2 > 0 \quad$ It is a minimum.
Functions of two or more variables

Often a function depends on more than one “independent” variable.

Functions of two variables can be represented as surfaces.

\[ f(x, y) = \text{dependent variable} \]
\[ x, y = \text{independent variables} \]
South Korea: Height vs. longitude and latitude

This is a topographical map.

The color indicates the height versus geographical coordinates.

What are extrema and how do we find them?

Height=dependent variable

Longitude=independent variable

Latitude=independent variable

Height(Longitude, Latitude)
Long Island home prices

26 of the most expensive zip codes in 2015!

Price = f(x,y,T) (location and age)
Example: A function of at least 4 variables

Temperature = T(Longitude, Latitude, Altitude, time).
Partial derivatives are slopes of tangents to multivariate functions in the direction of a given independent variable.

Calculation: As for any derivative, but holding all independent variables fixed except for one.
Partial derivatives: An example

Take a function (paraboloid):

\[ f(x, y) = x^2 + y^2 \]

The partial derivatives are:

\[ \frac{\partial f}{\partial x} = 2x \quad \frac{\partial f}{\partial y} = 2y \]

For a specific point:

\[ \frac{\partial f}{\partial x} \bigg|_{(2,-1)} = 4 \]
\[ \frac{\partial f}{\partial y} \bigg|_{(2,-1)} = -2 \]
Higher-order partial derivatives

Partial derivatives are functions of the same independent variables as the original function.

Higher-order partial derivatives can be defined, such as:

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x} \left( \frac{\partial f}{\partial x} \right)$$

Example: Two-dimensional Gaussian

$$f(x, y) = Ae^{-\left[ \frac{x^2}{2\sigma^2} + \frac{y^2}{2\sigma^2} \right]}$$
Estimating small changes

If we know a function in point $x_0$, we can estimate it nearby with a Taylor expansion:

$$f(x) = f(x_0) + \frac{1}{1!} \frac{df}{dx} \bigg|_{x=x_0} (x-x_0) + \frac{1}{2!} \frac{d^2f}{dx^2} \bigg|_{x=x_0} (x-x_0)^2 + \ldots$$

This is useful for estimating transcendental functions:

$$e^x = 1 + x + \frac{x^2}{2} + \ldots$$

For infinitesimal changes in $x$, the change in $f$ is the differential of $f$:

$$df(x) = \frac{df}{dx} \bigg|_{x=x_0} dx$$
Multivariate functions: Total differential

Taylor expansion near \([x_0, y_0]\):

\[
f(x, y) = f(x_0, y_0) + \Delta x \frac{\partial f}{\partial x}\bigg|_{x_0,y_0} + \Delta y \frac{\partial f}{\partial y}\bigg|_{x_0,y_0} + \frac{1}{2} \left[ \Delta x^2 \frac{\partial^2 f}{\partial x^2}\bigg|_{x_0,y_0} + \Delta y^2 \frac{\partial^2 f}{\partial y^2}\bigg|_{x_0,y_0} + 2\Delta x\Delta y \frac{\partial^2 f}{\partial x\partial y}\bigg|_{x_0,y_0} \right] + \ldots
\]

For infinitesimal changes we obtain the total differential:

\[
df = \sum_{i=1}^{N} \frac{\partial f}{\partial x_i}\bigg|_{x_j \neq i} \, dx_i
\]

How much does the function change if you take steps in all possible directions?

For two dimensions:

\[
df(x, y) = \frac{\partial f}{\partial x}\bigg|_{y} \, dx + \frac{\partial f}{\partial y}\bigg|_{x} \, dy
\]
Extrema: Where all partial derivatives are = 0

At extremum points, \( f \) is flat \textbf{in all directions} – it stays constant as \( x \) and \( y \) change infinitesimally.

This means that the differential of \( f \) is 0: \[
\frac{df}{dx} (x, y) = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy = 0
\]

Since \( dx \) and \( dy \) are independent, this is only assured if:

\[
\frac{\partial f}{\partial x} = 0 \quad \frac{\partial f}{\partial y} = 0
\]

More generally:

\[
\frac{\partial f}{\partial x_i} = 0 \quad \text{For all } i=1, 2, 3, \ldots
\]