Bringing thermodynamics to non-equilibrium microscopic processes

Miguel Rubi

Leverhulme Visiting Professor,
Department of Chemistry
Imperial College

http://www.ffn.ub.edu/webmrubi
Outline


• **L2. Mesoscopic non-equilibrium thermodynamics.** Dissipation at small scales. Chemical and biochemical reactions. Thermodynamics of single molecules and molecular motors. Ion translocation through protein channels.


Lecture 1

Non-equilibrium thermodynamics
Thermodynamics: fundamental questions

• The science of thermodynamics dates to an era of technological optimism, the mid-19th century, when steam engines were transforming the world and scientists such as Rudolf Clausius, Sadi Carnot, James Joule and Lord Kelvin developed a theory of energy and heat to understand how they work and what limited their efficiency.

• How much work can be extracted from a system? Free energy
• What is the work necessary to change the state of a system?
• What is the efficiency of that process?

• Thermodynamics sets up the way to calculate the dissipation (entropy production) of a process.

*J. M. Rubi, Scientific American, November 2008, p. 62*
How to characterize a system thermodynamically?

Two type of quantities:
- conserved quantities (E,V,N); extensive, E(A+B)=E(A)+E(B)
- the ones that determine the evolution of the system (T,p, µ); intensive.

Temperature:
Is a measure of the kinetic energy of the molecules;
The evolution of the state of a gas is the result of the action of driving forces and collisions between particles.

Equipartition law: in equilibrium, the mean kinetic energy of the molecules is given by

\[ \frac{3}{2} k_B T = \frac{1}{2} m \langle v^2 \rangle \]
\[ T = \frac{m}{3k_B} \langle v^2 \rangle \]
**Pressure:**

\[ p = \langle F \rangle / S \]

Pressures in DNA packaging and release from viral capsids: 20-30 atm.

Reaction rates depend on pressure.

**Chemical potential**

\[ A \rightarrow B; \quad \mu_A > \mu_B \]

\[ A \leftarrow B; \quad \mu_B > \mu_A \]

Two objects are in equilibrium when T, p and \( \mu \) are equal.
Heat, work and energy

- Heat is a form of energy that can be transformed into other forms of energy.
- First principle of thermodynamics: energy conservation law

\[ \Delta E = \Delta Q + \Delta W \]

- But the concept of work in thermodynamics has a more general meaning; work needed to create a state starting from another.

\[
\begin{align*}
\Delta W_{\text{mechanical}} &= -p \Delta V; -F \Delta x \\
\Delta W_{\text{chemical}} &= -\mu \Delta N \\
\Delta W_{\text{surface tension}} &= -\Sigma dA
\end{align*}
\]

Free energy

\[
\begin{align*}
\Delta W_{\text{ideal}} &= \Delta G \\
\Delta W - \Delta W_{\text{ideal}} &= \Delta W_{\text{lost}} = T \sigma \Delta t
\end{align*}
\]

Entropy production
Thermal radiation

\[ \Delta \dot{E}_c + \Delta \dot{E}_r + \dot{q}_e + \dot{W} = 0, \]
\[ \Delta \dot{S}_c + \Delta \dot{S}_r + \Delta \dot{S}_e = \Delta \dot{S}_{\text{dis}} \geq 0. \]

- \( \Delta \dot{S}_{\text{dis}} \) is the entropy production flux due to dissipation in the converter.
- Both equations are linked: \( \Delta \dot{S}_e = \dot{q}_e/T_2 \)
- Stationary regime: \( \Delta \dot{E}_c = \Delta \dot{S}_c = 0 \)


Efficiency

- First law efficiency:

\[ \eta_I = \frac{\dot{W}}{\dot{E}_r(T_1)} = \frac{\dot{W}_i - T_2 \Delta \dot{S}_{\text{dis}}}{\dot{E}_r(T_1)}. \]

Upper bound for the first law efficiency:

\[ \tilde{\eta} \equiv \frac{\dot{W}_i}{\dot{E}_r(T_1)} \geq \eta_I. \]

- Second law efficiency:

\[ \eta_{II} = \frac{\dot{W}}{\dot{W}_i} = \frac{\dot{W}_i - T_2 \Delta \dot{S}_{\text{dis}}}{\dot{W}_i}. \]

If the system works in ideal conditions, \( \Delta \dot{S}_{\text{dis}} = 0 \), one has \( \eta_{II} = 1 \).

- Note that

\[ \eta_{II} = \eta_I / \tilde{\eta}, \]

and we always have \( \eta_{II} \geq \eta_I \).
Work: stretching DNA

\[ m \frac{dv}{dt} = F_{\text{tot}} = F_{\text{friction}} + F_{\text{elastic}} \]

\[ m \frac{dv}{dt} = -\zeta v - k \left( x - v_{\text{opt}} t \right) \]

Fluctuations are important

\[ \Delta W = F \Delta x \]

\[ F \sim 10 \text{ pN} \]

\[ \Delta x \sim 400 \text{ nm} \]

\[ \Delta W \sim 10 k_B T \]
Elastic properties are different at small scales

C. Bustamante et al., Current Opinion in Structural Biology 2000, 10:279–285
Carbon nanotube-based motor

\[ F_T = \kappa_{zz} \frac{\partial T}{\partial z} \]

50-100 m/s ; 1K/nm; thermal force: pico Newtons
Entropy

• Is the first principle enough to determine the evolution of the systems?
• There are processes allowed by the first law that have never been observed.
• Ex. 1  Heat transfer from cold to hot
• Ex. 2 Reversible spontaneous reactions

A+B→C+D+Heat
A+B↔C+D

\[ ATP + H_2O \rightarrow ADP + P_i \]

\[ \Delta G = -32.5 \text{ KJ/mol} \]
Entropy

Experimental observation:

A transformation whose only final result is to transfer heat from a body at a given temperature to a body at a higher temperature in not possible.

To account for this fact one introduces the entropy

\[ \Delta S = \frac{\Delta Q}{T} \]

\[ \Delta Q_1 = -\Delta Q_2 \]

\[ \Delta S = \frac{\Delta Q_1}{T_1} + \frac{\Delta Q_2}{T_2} = \Delta Q_1 \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

\[ T_1 > T_2 \quad ; \quad \Delta Q_1 \leq 0 \quad ; \quad \Delta S \geq 0 \]

Chemical reaction

\[ A + B \rightarrow C + D \]

Adding more component A: destroys the equilibrium, displaces the reaction towards the right
Entropy and disorder

We can assign to a thermodynamical state a probability $P$. Therefore $S=f(P)$

$$S = f(P) = f(P_1P_2) = S_1 + S_2 = f(P_1) + f(P_2)$$

$$f(P) = k_B \ln P$$

$$S = k_B \ln P$$

Boltzmann entropy

$k_B = 1.38 \cdot 10^{-23} \text{ J} / \text{ K}$

**Molecule** composed of three parts 1, 2, 3 having the same energy:

**Configurations**: 123, 312, 231, 132, 213, 321

$P(123)=1/6$; more ordered, more information; $S$ smaller

$P(\{312, 231, 132, 213, 321\})=5/6$; more disordered; less information; larger $S$

Both entropies are equivalent
Non-equilibrium thermodynamics

Heat transfer:

- Energy supplied is used to increase the momentum of the molecules; kinetic energy transfer.
- System is not in equilibrium
- What is the temperature of the system? In equilibrium all parts are at the same $T$; in our situation $T$ varies along the system: $T(x)$

Observation: $T$ varies continuously along the system.
Conservation laws

Heat conduction

\[ \frac{\Delta e_i}{\Delta t} = -J_i + J_{i-1} \]

\[ E = e_1 + \ldots + e_{i-1} + e_i + e_{i+1} + \ldots + e_n \]

output, input

Small-cell and time limits:

\[ \frac{\partial e}{\partial t} = -\frac{\partial J}{\partial x} \]
In 2, the cells contain many particles and can be assimilated to a small thermodynamic system in equilibrium.

\[ \rho = \frac{\Delta m}{\Delta V} \] (small \( \Delta V \)'s)

1: Large fluctuations
2: No variation
3: Smooth variation

Local equilibrium
Small-scale systems

- The energy may contain contributions not present when the number of particles becomes very large. Small cluster composed of $N$ particles

$$G = \mu N + \nu N^{2/3} = \mu N \left(1 + \frac{\nu}{\mu} N^{-\frac{1}{3}}\right)$$

- Unavoidable presence of fluctuations at such scales which can be large. These fluctuations scale with $1/\sqrt{N}$; become negligible for large $N$. 
Heat conduction

\[ de = dq = T ds \]

\[ \frac{ds}{dt} = \frac{1}{T} \frac{de}{dt} = -\frac{1}{T} \frac{\partial J_q}{\partial x} = -\frac{\partial}{\partial x} \left( \frac{1}{T} J_q \right) + J_q \frac{\partial}{\partial x} \left( \frac{1}{T} \right) \]

\[ J_s: \text{entropy flux} \quad \sigma: \text{entropy production} \]

\[ \sigma = J_q \frac{\partial}{\partial x} \left( \frac{1}{T} \right) = -\frac{1}{T^2} J_q \frac{\partial T}{\partial x} \]

\[ J_q = -\frac{L}{T^2} \frac{\partial T}{\partial x} = -\lambda \frac{\partial T}{\partial x} \]

\textbf{Fourier's law}
Fluxes and forces

<table>
<thead>
<tr>
<th>process</th>
<th>flux</th>
<th>force</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat</td>
<td>$\vec{J}_q$</td>
<td>$-\frac{1}{T^2}\nabla T$</td>
</tr>
<tr>
<td>diffusion</td>
<td>$\vec{J}$</td>
<td>$-\frac{1}{T}\nabla \mu$</td>
</tr>
<tr>
<td>reaction</td>
<td>$r$</td>
<td>$-\frac{1}{T} A$</td>
</tr>
</tbody>
</table>

Second law:

$$L_{11}, L_{22} \geq 0$$

$$(L_{12} + L_{21})^2 < 4L_{11}L_{22}$$

General:

$$\sigma = -\vec{J}_q \cdot \frac{1}{T^2}\nabla T - \vec{J} \cdot \frac{1}{T}\nabla \mu - r \frac{1}{T} A$$

Onsager reciprocal relations:

$$J_1 = L_{11}x_1 + L_{12}x_2$$

$$J_2 = L_{21}x_1 + L_{22}x_2$$

$$L_{12} = L_{21}$$
- Heat conduction in a solid or in a liquid in the absence of convection:

\[ \sigma = -\frac{1}{T^2} \vec{J}_q \cdot \nabla T \]

\[ \vec{J}_q = -\frac{L_q}{T^2} \nabla T = -\lambda \nabla T \]  

Fourier’s law

- Mass diffusion:

\[ \vec{J}_d = -\frac{L_d}{T} \nabla c = -D \nabla c \]  

Fick’s law

- Chemical reaction:

\[ J_r = -\frac{L_r}{T} A = -\frac{L_r}{T} (\mu_2 - \mu_1) \]  

Law of mass action  
(up to linear order)

- Viscous flow

\[ \Pi = -2\eta \nabla \nu \]  

Navier-Stokes equation
Active transport:

Motion of the ions against a concentration gradient

\[ ATP + H_2O \rightarrow ADP + P_i \]

\[ \Delta G = -32.5 \text{ KJ/mole} \]

Reaction coordinate

\[ T \sigma = -J \nabla \mu - rA \]

\[ J = -L_{dd} \nabla \mu - L_{dr} \left( \mu_{ADP+P_i} - \mu_{ATP+H_2O} \right) \]

Coupling between diffusion and chemical reaction is only possible in 1d (channel, pore,..); geometry matters
Soret and Dufour effects

Coupling between heat conduction and diffusion

\[ \sigma = -\tilde{J}_q \cdot \frac{1}{T^2} \nabla T - \tilde{J} \cdot \frac{1}{T} \nabla \mu \]

\[ \tilde{J}_q = -\frac{L_{qq}}{T^2} \nabla T - \frac{L_{qd}}{T} \nabla \mu \]

\[ \tilde{J}_d = -\frac{L_{dq}}{T^2} \nabla T - \frac{L_{dd}}{T} \nabla \mu \]

Thermoelectric effects

Coupling between heat conduction and electrical current

Others...

Summary

• NET provides a description of irreversible processes taking place in large-scale systems.
• Linear relations between fluxes and forces.
• Deterministic description in terms of mean values; absence of fluctuations.