

MATE 664 Lecture 02

Introduction to Irreversible Thermodynamics

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Recap of Lecture 01 (Big Picture)

Key ideas from last lecture:

- Thermodynamics tells us **whether** a process can occur
- Kinetics tells us how **fast** it occurs
- Equilibrium depends on time scales, not perfection
- Free energy change ΔG^0 determines spontaneity
- Activation barrier ΔG^* controls rates

Recap: Equilibrium Is a Time-Scale Concept

- Equilibrium when

$$\tau_{\text{observation}} \gg \tau_{\text{relaxation}}$$

- Many materials are metastable, not unstable
- Diamond vs graphite is a kinetic story, not thermodynamic failure

Recap: Entropy Revisited

- Entropy is **not disorder**
- Entropy measures number of accessible **microstates**
- Statistical view:

$$S = k_B \ln \Omega$$

Learning Outcomes

After this lecture, you will be able to:

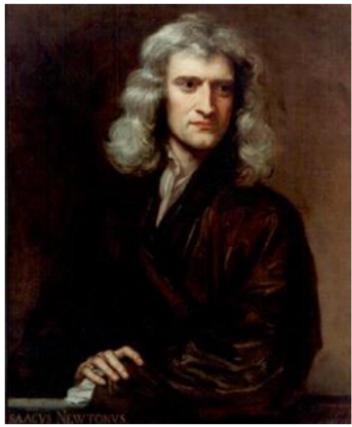
1. Explain why classical thermodynamics fails for real kinetic processes
2. Define entropy production and irreversible processes
3. Relate macroscopic fluxes to thermodynamic driving forces
4. Apply Onsager's linear response framework
5. Interpret irreversible thermodynamics from a microscopic viewpoint

Crash Course on Statistical Mechanics (1)

Part of the introductions are adapted from MAT E 374 by Dr. Hao Zhang

Dynamics from Newton & Laplace point of view:

- Transition from state A to B is **deterministic**
- We just need to know $\{\mathbf{x}_i, \mathbf{v}_i, F_{ij}\}$



NEWTON: $F=ma$

LAPLACE:

Nous devons donc envisager l'état présent de l'univers comme l'effet de son état antérieur et comme la cause de celui qui va suivre. Une intelligence qui, pour un instant donné, connaîtrait toutes les forces dont la nature est animée et la situation respective des êtres qui les composent, si d'ailleurs elle était assez vaste pour soumettre ces données à l'Analyse, embrasserait dans la même formule les mouvements des plus grands corps de l'univers et ceux du plus léger atome : rien ne serait incertain pour elle, et l'avenir, comme le passé, serait présent à ses yeux.



Figure 1: Newtonian dynamics in a nutshell

Crash Course on Statistical Mechanics (2)

Why can't we determine the system state using Newtonian Dynamics (yet)?

- Astronomical numbers of microstates
- Limitation of computational power
- Waste of computational power

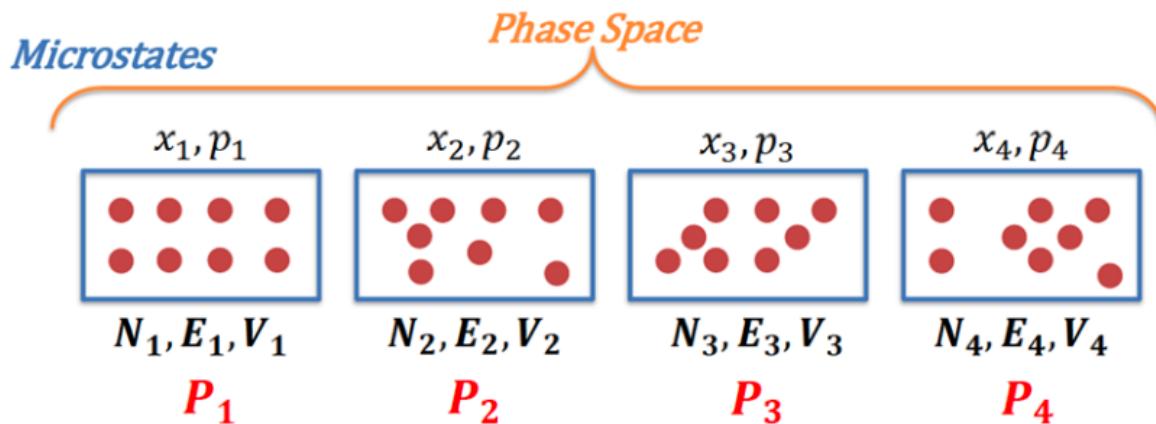
What is the alternative?

- Deterministic → Probabilistic
- *How much computation is enough?*

Crash Course on Statistical Mechanics (3)

Let's reintroduce the microscopic picture by Boltzmann

Let us consider, a one-component macroscopic system:



Which microstate would the system choose?

It won't choose: it will explore all available microstates according to a specific probability distribution...

Crash Course on Statistical Mechanics (4)

- **Microstate:** a state in the phase space $\{\mathbf{x}_i, \mathbf{p}_i\}$
- **Macrostate:** a specification of macroscopic constraints (e.g. $\langle E, V, N \rangle$) that corresponds to many microstates
- **Ensemble:** a set of constraints like $\langle E, V, N \rangle$ describing the system

i Central principle linking macrostate and microstates:

The observed macroscopic thermodynamic property A_{obs} is an **ensemble average** of all possible microstates i

$$A_{obs} = \langle A \rangle = \sum_i A_i p_i$$

Crash Course on Statistical Mechanics (5)

Consider a *canonical ensemble* (constant N, V, U) ¹

- Inner system (I): $U_I, \Omega(U_I)$
- Reservoir system (R): $U_R, \Omega(U_R)$
- Total system (universe, T): $U_T = U_I + U_R, \Omega(U_T) = \Omega(U_I) \times \Omega(U_R)$
- $U_R \gg U_I$

I and R can only exchange internal energy, not particles or volume.

Q: The total internal energy of the universe U_T is fixed. How do the inner and reservoir systems balance their energies?

Crash Course on Statistical Mechanics (6)

Let's first see the equilibrium state.

- Assume at e.q., we have $U_I = U_I^0$
- Probability of inner energy follows how many states in the reservoir they can exchange with:

$$P(U_I) \propto \Omega(U_T - U_I^0)$$

- Since $U_T \approx U_R \gg U_I^0$, we can use Taylor series for $\Omega(U_T - U_I^0)$:

$$\ln \Omega(U_T - U_I^0) = \ln \Omega(U_T) - \frac{\partial \ln \Omega}{\partial U} \bigg|_{U=U_T} \cdot U_I^0 + \dots$$

¹Adapted from Green, Kinetics Transport, and Structure in Hard and Soft Materials, Ch 1

Crash Course on Statistical Mechanics (7)

- We know the Boltzmann equation $S = k_B \ln \Omega$

$$\ln P(U_I^0) \propto \ln \Omega(U_T) - \frac{\partial S_T}{k_B \partial U} \bigg|_{U=U_T} \cdot U_I^0$$

Recall the classical thermodynamic relation:

$$dU = TdS - pdV$$

We have $\frac{\partial S}{\partial U} \bigg|_V = \frac{1}{T}$, therefore

$$P(U_I^0) \propto \Omega(U_T) \exp\left(-\frac{U_I^0}{k_B T}\right)$$

This leads the famous **Boltzmann distribution**

Crash Course on Statistical Mechanics (8)

What if we're not at equilibrium?

T_I and T_R may be two distinct values.

- We will apply *local equilibrium* assumption here
- One postulate for stat. mech. is that the entropy of the universe always **increases**.
- We go further by say the equilibrium **maximizes** the universe entropy

$$\left(\frac{\partial \ln \Omega(U_T)}{\partial U_I} \right)_{N,V,U} = 0$$

- *Can we make sure it is the maximum?*
- What is the sign of $\partial^2 S / \partial U^2$?

Crash Course on Statistical Mechanics (9)

$$\left(\frac{\partial \ln \Omega(U_I)}{\partial U_I} \right)_{N,V,U} + \left(\frac{\partial \ln \Omega(U_R)}{\partial U_I} \right)_{N,V,U} = 0$$

Use the relation $\partial U_I = -\partial U_R$

$$\left(\frac{\partial \ln \Omega(U_I)}{\partial U_I} \right)_{N,V,U} = \left(\frac{\partial \ln \Omega(U_R)}{\partial U_R} \right)_{N,V,U}$$

Apply Boltzmann equation

$$T_I^{-1} = T_R^{-1}$$

Yay! This is something we know, temperature at equilibrium.

What Have We Observed So Far?

- Probability distribution **at equilibrium** follows Boltzmann distribution (for canonical ensemble)
- Equilibrium is a consequence of maximizing entropy of the universe
- We can locally apply the equilibrium thermodynamics to describe kinetic process (though we don't know how fast yet)

Formal Framework

In Onsager's Irreversible Thermodynamics, for any thermodynamic parameter X , we define

- **Affinity F** : the influence of X_i to the universe entropy

$$F_i = \frac{\partial S}{\partial X_i}$$

- **Flux J** : the change of parameter X_i (or density of it) per unit time

$$J_i = \frac{dX_i}{dt}$$

- **Kinetic Coefficient L_{ij}** : influence of flux type i by affinity type j (linear term).

$$L_{ij} = \frac{\partial J_i}{\partial F_j}$$

Postulate 1: Local Equilibrium

- It is generally possible to use principles of the **continuum limit** to define meaningful, useful, local values of various thermodynamics quantities, e.g., chemical potential μ_i .
- Useful kinetic theories can be developed by assuming a functional relationship between the rate of a process and the local departure from equilibrium (“**driving force**”).

Postulate 2: Entropy Production

Irreversible Process is An Increase of Entropy in the Universe

$$\frac{dS}{dt} = \sum_i \frac{\partial S}{\partial X_i} \frac{\partial X_i}{\partial t} = \sum_i F_i J_i$$

- Entropy can be created in the universe
- Entropy can flow between micro-systems
- Rate of entropy production (entropy generation + flow) must be positive

Postulate 3: Linearity

- The relation between J and X can be linearly described (resistive system).
- Flux is only dependent on the affinity **at the same time**

$$J_1 = L_{11}F_1 + L_{12}F_2 + \dots + L_{1\Sigma}F_\Sigma \quad (1)$$

$$\vdots \quad (2)$$

$$J_\Sigma = L_{\Sigma 1}F_1 + L_{\Sigma 2}F_2 + \dots + L_{\Sigma\Sigma}F_\Sigma \quad (3)$$

$$(4)$$

Or in vector term

$$\mathbf{J} = \mathbf{L} \cdot \mathbf{F}$$

- Coefficient L_{ii} is called **direct kinetic coefficient**
 - Affinity F_i is called **conjugate driving force** w.r.t. J_i
- Coefficient $L_{ij}(i \neq j)$ is called **coupling coefficient**

Postulate 4: Reciprocity

Onsager propose that

$$L_{ij} = L_{ji}$$

This is a key component in material kinetics!



Summary: Irreversible Thermodynamics in One Slide

- Irreversible processes are driven by **thermodynamic forces**
- Each force generates a corresponding **flux**
- Near equilibrium, fluxes depend **linearly** on forces
- Empirical transport laws (Fourier, Ohm, Fick) are special cases of:

$$J_i = \sum_j L_{ij} F_j$$

- Onsager reciprocity enforces symmetry:

$$L_{ij} = L_{ji}$$