Lecture 12: Non-equilibrium thermodynamics.

Classical thermodynamics: Conversion of heat and work in systems that are in a state of equilibrium.

What does equilibrium mean?

(i) Does not depend on its history.
(ii) No time dependence
(iii) No net transport of heat, mass, ... ⟹ no currents, no fluxes.

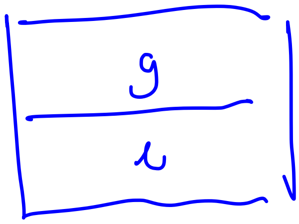
Second law of thermodynamics defines arrow of time.

Spontaneous process: The entropy of an isolated system will not decrease.

Thermodynamic potential E (no work or heat exchange)
$\xrightarrow[\text{law}]{\text{2nd}}$ Energy is minimal, entropy is maximal.

More broadly: System in thermodynamic equilibrium
all intensive thermodynamic variables are constant in space & time

E.g



$T_g = T_l$

$P_g = P_l$

$\mu_g = \mu_l$.

In non-equilibrium state, intensive variables are not constant.

⤳ spatial gradients in intensive variables, s.t. system moves towards a state of thermodynamic equilibrium.

⤳ currents & fluxes:

$\nabla p \Leftrightarrow$ momentum transport. ("volume")
$\nabla \mu \Leftrightarrow$ mass transport.
$\nabla T \Leftrightarrow$ heat (entropy) transport

"roughly".

Axiomatic thermodynamics.

Defines thermodynamic state variables $(T, E, S, \dots)$

$\rightsquigarrow$ depend only on the thermodynamic state.

Collection of state variables define thermodynamic state

+ equations of state which relate various state variables, e.g. $\beta p = \rho$ (ideal gas)

Intensive variables: $\vec{f} := (p, \mu, \gamma, \vec{E}, \vec{B}, \dots)$ "generalised forces"

Extensive variables: $\vec{X} = (-V, N, A, \vec{P}, \vec{M}, \dots)$ "generalised displacements".

Since product is a form of work.

Laws of thermodynamics.

0^{th} law Systems A & B are in thermal equilibrum $\Leftrightarrow T_A = T_B$.

Property is transitive: A in eq. with B and B in equilibrium with C

$\Rightarrow T_A = T_C$, A is in equilibrium with C

(relevant for thermometers) Applies also to mechanical and chemical equilibrium.

1^{st} law There exists a state function E called internal energy which is additive and extensive.

E is conserved: $dE = \text{đ}Q + \text{đ}W$

Q: heat absorbed by the system.
W: work done on the system.

Configurational work: $\text{đ}W = \vec{f} \cdot d\vec{X}$.

2^{nd} law There exists a state function S called the entropy. S is extensive and additive. Since it is a state function dS is exact.

S is postulated to be a monotonically increasing function of E.

For isolated system: $S = S(E, \vec{x})$

$$\Delta S = \int_a^b dS \geq 0$$ for any process connecting thermodynamic states a and b.

where equality holds for reversible processes, and strict inequality for spontaneous (i.e. irreversible) processes.

Corrollary Consider $dS = \left(\frac{\partial S}{\partial E}\right)_{\vec{x}} dE + \left(\frac{\partial S}{\partial \vec{x}}\right)_E \cdot d\vec{x}$. $\Big\} \Rightarrow$

For reversible process: $dE = (đQ)_{rev} + \vec{f} \cdot d\vec{x}$

$$dS = \left(\frac{\partial S}{\partial E}\right)_{\vec{x}} (đQ)_{rev} + \left[\left(\frac{\partial S}{\partial \vec{x}}\right)_E + \left(\frac{\partial S}{\partial E}\right)_{\vec{x}} \vec{f}\right] \cdot d\vec{x}. \quad (*)$$

For adiabatic reversible process: $(đQ)_{rev} = 0$.

But $(*)$ must hold for all reversible processes, thus: $\left(\frac{\partial S}{\partial \vec{x}}\right)_E = -\left(\frac{\partial S}{\partial E}\right)_{\vec{x}} \vec{f}$

Since S monotonically increases with E: $\left(\frac{\partial S}{\partial E}\right)_{\vec{x}} =: \frac{1}{T} > 0$

Therefore: $\left(\frac{\partial S}{\partial \vec{x}}\right)_E = -\frac{\vec{f}}{T}$.

So we conclude for reversible processes: $dS = \frac{1}{T} dE - \vec{f}/T \cdot d\vec{x}$

$$\Leftrightarrow dE = T dS + \vec{f} \cdot d\vec{x}.$$

In other words S is the exact differential corresponding to heat transport with temperature being the integrating factor.

See Chandler $\quad S$ maximal for isolated system $\Leftrightarrow E$ minimal.

$\Rightarrow \vec{f}$ must be constant in space & time in equilibrium. (eq. condition)

and $\frac{\partial \vec{f}}{\partial \vec{x}} > 0$ (stability condition)

3rd law S approaches a constant value as the absolute temperature reaches zero Kelvin.

$\Leftrightarrow$ $T=0$ cannot be reached in finite number of processes.

$\vec{f}$ in equilibrium constant in space and time. What about nonequilibrium?

Fundamental assumption: Even for systems that are globally out of equilibrium, locally it acquires equilibrium so fast that we can define local versions of the intensive variables.

$\Rightarrow$ Non-eq. thermodynamics focuses on time scales much longer than the time scales of the establishment of local equilibrium.

Recall: $dS = \frac{1}{T} dE - \frac{\vec{f}}{T} \cdot d\vec{X}$

Note $\frac{1}{T}$ is conjugate to E

$-\frac{\vec{f}}{T}$ is conjugate to $\vec{X}$

$\Rightarrow$ We conjecture that gradients in $\frac{1}{T}$ cause energy transport, and gradients in $\frac{\vec{f}}{T}$ cause transport of $\vec{X}$.

Let's focus on an isolated system.

E and N are conserved.

So we can define local quantities

$\epsilon = \epsilon(\vec{r},t)$ and $\rho = \rho(\vec{r},t)$.

For now we don't take into account balance of linear momentum. (no convection)

Continuity equations:

$$\frac{\partial \epsilon}{\partial t} + \nabla \cdot \vec{J}_\epsilon = 0$$

(energy conservation) $\vec{J}_\alpha$: flux.

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{J}_\rho = 0.$$

(particle number conservation)

We impose the so-called phenomenological laws:

$$J_i = \sum_k L_{ik} \nabla \phi_k.$$

L_{ik} : phenomenological coefficients

F_k : thermodynamic forces.

So we find:

$$\vec{J}_\rho = L_{\rho\rho} \nabla\left(-\frac{\mu}{T}\right) + L_{\rho\epsilon} \nabla\left(\frac{1}{T}\right)$$

$$\vec{J}_\epsilon = L_{\epsilon\rho} \nabla\left(-\frac{\mu}{T}\right) + L_{\epsilon\epsilon} \nabla\left(\frac{1}{T}\right).$$

cross coefficients.

Soret effect:
coupling between mass & heat transport.

Temperature gradient $\Leftrightarrow$ concentration gradient.

Onsager (Nobel prize, 1968) : $L_{ij} = L_{ji}$. (we will prove it later).

Connection with empirical transport laws.

E.g.:

$\vec{J}_\rho = -D \nabla \rho$. $\quad$ $D\ [m^2 s^{-1}]$: diffusivity or diffusion constant.

Fick's first law of diffusion. $\quad$ Isothermal particle transport.

Valid for dilute gases / dilute solutions.

How it connects to $\vec{J}_\rho = L_{\rho\rho} \nabla\left(-\frac{\mu}{T}\right)$?

For dilute gases / dilute solutions $\beta\mu = \ln \rho \mathcal{V}$

$\Rightarrow L_{\rho\rho} = \frac{D\rho}{k_B}$.

When inserted in continuity equation: $\frac{\partial \rho}{\partial t} = D \nabla^2 \rho$.

Fick's second law.

Entropy production.

Consider general system (not necessarily isolated).

$$dS = dS_i + dS_e$$

dS_e $\leftarrow$ entropy supplied to the system by its surroundings.

dS_i: entropy produced inside the system.

Recall: $dS_i = 0$ for reversible (equilibrium) transformations.

$dS_i > 0$ for irreversible.

dS_e can be positive, negative, or zero depending on how system interacts with surroundings.

Adiabatic systems: $dS_e = 0 \Rightarrow dS \geq 0$ for adiabatically insulated system.

For closed system: $dS_e = \frac{đQ}{T}$ (Carnot-Clausius theorem)

$$dS \geq \frac{đQ}{T}$$

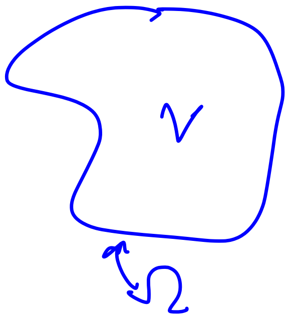
In irreversible thermodynamics: $dS_i > 0$

Central goal is to relate this contribution to the entropy production.

$$S = \int_V d\vec{r}\, s(\vec{r},t).$$

$$\frac{dS_e}{dt} = -\int_\Omega \vec{J}_s \cdot d\vec{\Omega}$$

entropic flux. per unit area per unit time.



$$\frac{dS_i}{dt} = \int_V d\vec{r}\, \sigma$$

entropy source strength or "entropy production".

Using Gauß law, we find:

$$\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \sigma$$

$\sigma \geq 0$ (entropy production must be positive even locally, strong conjecture).

Locally: $T\,ds = de - \sum_{k=1}^{n} \mu_k \, d\rho_k.$ Assume this equation is valid for a volume element followed along its centre of gravity motion

$$T\frac{ds}{dt} = \frac{d\epsilon}{dt} - \sum_{k=1}^{n} \mu_k \frac{d\rho_k}{dt}.$$

For now no convection: $\frac{d}{dt} = \frac{\partial}{\partial t}$.

$$\Rightarrow \frac{\partial s}{\partial t} = -\frac{\nabla\cdot\vec{J}_\epsilon}{T} + \frac{1}{T}\sum_{k=1}^{n}\mu_k \nabla\cdot\vec{J}_k.$$

$$= -\nabla\cdot\left[\frac{\vec{J}_\epsilon - \sum_k \mu_k \vec{J}_k}{T}\right] + \vec{J}_\epsilon\cdot\nabla\left(\frac{1}{T}\right)$$

$$- \frac{1}{T}\sum_{k=1}^{n}\vec{J}_k\cdot\nabla\left(\frac{\mu_k}{T}\right)$$

Comparison to the entropy balance gives:

$$\vec{J}_s = \frac{1}{T}\left(\vec{J}_\epsilon - \sum_{k=1}^{n}\mu_k\vec{J}_k\right)$$

$$\sigma = \vec{J}_\epsilon\cdot\nabla\left(\frac{1}{T}\right) - \sum_{k=1}^{n}\vec{J}_k\cdot\nabla\left(\frac{\mu_k}{T}\right).$$

Separation into div + source term is constrained s.t. $\sigma = 0$ in equilibrium.

and that it must be invariant under a Galilei transformation.

Furthermore, $\frac{dS}{dt} \geq -\int_{\partial\Omega}\frac{\vec{J}_\epsilon}{T}\cdot d\vec{\Omega}$.

Together with phenomenological laws, we see that:

$$\sigma = \sum_i J_i F_i = \sum_{i,k} L_{ik} F_i F_k.$$

F_i: generalised forces.

J_i: generalized fluxes.

$\Rightarrow$ $\underline{\underline{L}}$ must be positive definite; and together with Onsager reciprocity $\underline{\underline{L}} = \underline{\underline{L}}^T$.

The only thing left to prove is Onsager reciprocity.

For this we need the so-called Einstein fluctuation theory.

Einstein fluctuation theory

We write the local entropy as $ds = \vec{\phi} \cdot d\vec{\rho}$ ← generalised densities.

↑ generalised potentials

So: $\vec{\rho} = (\epsilon, \rho_1, \ldots, \rho_n, \ldots)$

$\vec{\phi} = (T^{-1}, -T^{-1}\mu_1, \ldots, -T^{-1}\mu_n, \ldots)$

Let $\Omega(E)$ denote the number of microstates of an isolated system. (microcanonical ensemble).

Consider $\Omega(E, \vec{\rho}) < \Omega(E)$.

Fundamental assumption of statistical mechanics:

$$\left.\begin{aligned} P(E,\vec{\rho}) &= \frac{\Omega(E,\vec{\rho})}{\Omega(E)} \\ S(E,\vec{\rho}) &= k_B \ln \Omega(E,\vec{\rho}) \end{aligned}\right\} \Rightarrow P(E,\vec{\rho}) = \frac{1}{\Omega(E)} \exp\left[-\frac{S(E,\vec{\rho})}{k_B}\right].$$

Second law: entropy is maximal in equilibrium. $\vec{\rho} = \vec{\rho}_{eq}$.

Define $\vec{\alpha} = \vec{\rho} - \vec{\rho}_{eq}$. (small fluctuation away from equilibrium)

Then: $S(E,\vec{\rho}) = S(E,\vec{\rho}_{eq}) - \frac{1}{2}\vec{\alpha} \cdot \underline{\underline{g}} \cdot \vec{\alpha} + \ldots$

where $\underline{\underline{g}} = -\frac{\partial}{\partial \vec{\rho}}\left(\frac{\partial S}{\partial \vec{\rho}}\right)\Big|_{\vec{\rho}=\vec{\rho}_{eq}}$; $g_{\alpha\beta} = -\frac{\partial^2 S}{\partial\rho_\alpha \partial\rho_\beta}\Big|_{\vec{\rho}=\vec{\rho}_{eq}}$.

Note that $\underset{=}{g}$ must be positive definite (second law).

$$\underset{=}{g} = \underset{=}{g}^T \quad (S \text{ is a state function}).$$

Note furthermore $g_{\alpha\beta} = g_{\beta\alpha} \Rightarrow$ Maxwell relations.

Assuming that $-\infty < \alpha_k < \infty$, we have that

$$P(E, \vec{p}) = P(\vec{\alpha}) = \sqrt{\frac{\det \underset{=}{g}}{(2\pi k_B)^n}} \exp\left(-\frac{\vec{\alpha}\cdot\underset{=}{g}\cdot\vec{\alpha}}{2k_B}\right).$$

This is a Gaussian distribution, so:
$$\langle \alpha_i \alpha_j \rangle = k_B \, g^{-1}_{ij}$$
$$\langle \vec{\alpha}\vec{\alpha} \rangle = k_B \, \underset{=}{g}^{-1}$$

which follows also from $\left\langle \left(\frac{\partial \Delta S}{\partial \alpha_i}\right) \alpha_j \right\rangle = -k_B \delta_{ij}$ (exercise).

To proceed, we need to extend above formalism to include temporal fluctuations.

Since $\Gamma = \Gamma(t)$, where $\Gamma = (\vec{p}^N, \vec{r}^N) \Rightarrow \vec{\alpha} = \vec{\alpha}(t)$.

Recall time evolution is given by

$$\frac{\partial \vec{p}_i}{\partial t} = -\frac{\partial H}{\partial \vec{r}_i}$$

$$\frac{\partial \vec{q}_i}{\partial t} = +\frac{\partial H}{\partial \vec{p}_i}$$

with 6N initial conditions.

Note that these equations are invariant under $t \longrightarrow -t$, $\vec{p}^N \longrightarrow -\vec{p}^N$.

This is called time-reversal invariance.

Now consider joint probability distribution that $\vec{\alpha} = \vec{\alpha}(0)$
$\vec{\alpha}' = \vec{\alpha}(t)$

$$P(\vec{\alpha}, \vec{\alpha}'; t) = \int_{(E, E+dE)} d\Gamma \int d\Gamma' \, P(\Gamma, \Gamma'; t)\, \delta(\vec{\alpha} - \vec{\alpha}(\Gamma))\, \delta(\vec{\alpha}' - \vec{\alpha}(\Gamma'))$$

$$\Gamma = (\vec{p}^N(0), \vec{r}^N(0)) \qquad \Gamma' = (\vec{p}^N(t), \vec{r}^N(t)).$$

where it is implied that integrations of Γ and Γ' are confined to energy shell $(E, E+dE)$

Now consider conditional probability $P(\vec{\alpha} | \vec{\alpha}'; t)$
Probality to have $\vec{\alpha}'$ at time t given that system was at $t=0$ at $\vec{\alpha}$.

Then $P(\vec{\alpha}, \vec{\alpha}'; t) = P(\vec{\alpha} | \vec{\alpha}'; t)\, P(\vec{\alpha})$

$$= \int_{(E, E+dE)} d\Gamma \int d\Gamma' \, P(\Gamma)\, P(\Gamma | \Gamma'; t)\, \delta(\vec{\alpha} - \vec{\alpha}(\Gamma))\, \delta(\vec{\alpha}' - \vec{\alpha}(\Gamma'))$$

$$= \frac{1}{\Omega} \int_{(E, E+dE)} d\Gamma \int d\Gamma' \, P(\Gamma | \Gamma'; t)\, \delta(\vec{\alpha} - \vec{\alpha}(\Gamma))\, \delta(\vec{\alpha}' - \vec{\alpha}(\Gamma'))$$

Because of microscropic time reversibility:

$$P(\vec{r}^N, \vec{p}^N | \vec{r}'^N, \vec{p}'^N; t) = P(\vec{r}^N, -\vec{p}^N | \vec{r}'^N, -\vec{p}'^N; -t)$$
$$= P(\vec{r}'^N, -\vec{p}'^N | \vec{r}^N, -\vec{p}^N; t)$$

causality

This expression shows that if we reverse momenta, particles retrace their former path.

Let's apply this expression to

$$P(\vec{\alpha})P(\vec{\alpha}|\vec{\alpha}';t) = \frac{1}{\Omega}\int_{(E,E+dE)} d\Gamma \int d\Gamma' \; P(\Gamma'|\Gamma;t)\,\delta(\vec{\alpha}-\vec{\alpha}(\Gamma))\,\delta(\vec{\alpha}'-\vec{\alpha}(\Gamma'))$$

Here, we used that $(\vec{r}^N,\vec{p}^N) \to (\vec{r}^N, -\vec{p}^N)$

$(\vec{r}'^N,\vec{p}'^N) \to (\vec{r}'^N, -\vec{p}'^N)$.

and that $\vec{\alpha}$ variables are even functions of momenta, i.e.

$$\vec{\alpha}(\vec{r}^N,\vec{p}^N) = \vec{\alpha}(\vec{r}^N,-\vec{p}^N)$$

$\Rightarrow P(\vec{\alpha})P(\vec{\alpha}|\vec{\alpha}';t) = P(\vec{\alpha}')P(\vec{\alpha}'|\vec{\alpha};t)$. (detailed balance)

From detailed balance one can show that:

$$\langle \vec{\alpha}(0)\vec{\alpha}(t)\rangle = \langle \vec{\alpha}(t)\vec{\alpha}(0)\rangle$$

$$\Rightarrow \langle \vec{\alpha}(0)(\vec{\alpha}(t)-\vec{\alpha}(0))\rangle = \langle (\vec{\alpha}(t)-\vec{\alpha}(0))\vec{\alpha}(0)\rangle$$

Divide by t and take $t\to 0$

$$\left\langle \vec{\alpha}\,\frac{\partial\vec{\alpha}}{\partial t}\right\rangle = \left\langle \frac{\partial\vec{\alpha}}{\partial t}\,\vec{\alpha}\right\rangle \quad (*) \quad \forall t$$ since in equilibrium time-translation invariance.

Onsager regression hypothesis: Decay or regression of spontaneous fluctuations is governed by the same laws as macroscopic flows that occur in response to an external perturbation.

$$\Rightarrow \frac{\partial \alpha_i}{\partial t} = \sum_k L_{ik}\left(\frac{\partial \Delta S}{\partial \alpha_k}\right)$$

$(*)$

$$\left\langle \frac{\partial \Delta S}{\partial \alpha_i}\alpha_j\right\rangle = -k_B\delta_{ij}$$

$\Rightarrow L_{ij} = L_{ji}$ ☐.

Can be generalized to variables that are odd under momentum reversal (see de Groot, Mazur)