Thermodynamics. Analysis of a single system.

- *Thermodynamic properties* = volume, pressure, temperature, *etc*.
- *Thermodynamic equilibrium state* = state of single system in which thermodynamic properties are constant.
- *Thermodynamic entropy* (property of a state f) = change in heat to temperature for a reversible process that begins in state i and ends in state f:

$$S_T(f) = {}_R\int_i^f \frac{\delta Q_R}{T}$$

- Claim: $S_T(f)$ takes maximum value when f is a thermodynamic equilibrium state.

Boltzmannian Statistical Mechanics. Analysis of a *single* multiparticle system.

- *Thermodynamic properties* = macroproperties that reduce to microproperties (position, momentum) of particles.
- Point X in Ω = possible *microstate* of system; subset Γ of Ω = possible *macrostate* of system.
  - Macroproperty = a function $f : \Omega \rightarrow \mathbb{R}$.
- *Boltzmann equilibrium macrostate* = macrostate of single system with greatest phase space volume.
  - No guarantee that system will remain in it (no guarantee that macroproperties of this state remain constant).
- *Boltzmann entropy* (property of a macrostate Γ) = size of macrostate Γ:

$$S_B(\Gamma) = k \log|\Gamma|$$

  - Or: $S_B(\Gamma_D) = k \log(G(D)) + \textit{const.}$, where $G(D)$ is the probability of the Boltzmann distribution D corresponding to the macrostate Γ_D.
  - Or: $S_B(\Gamma_D) = -k \sum n_i \log n_i + \textit{const.}$, where n_i is the number of microstates in cell w_i.
  - Or: $S_B(\Gamma_D) = -Nk \sum p_i \log p_i + \textit{const.}$, where p_i is the probability of finding a microstate in cell w_i.

Gibbsian Statistical Mechanics. Analysis of an *ensemble* of infinitely many copies of a multiparticle system.

- Point x in Ω = microstate of a member of ensemble.
- State of entire ensemble = Gibbs distribution $\rho(x, t)$ on Ω.
  - $\int_S \rho(x,t)\,dx$ = probability at time t of finding the system's microstate in region S.
  - Ensemble average of f: $\langle f \rangle = \int_\Omega f(x)\rho(x,t)\,dx$
- *Statistical equilibrium distribution* = stationary distribution ρ (doesn't change in time).
  - $\langle f \rangle$ is constant just when ρ is stationary. So, if thermodynamic properties are represented by ensemble averages, then they do not change in time for stationary distributions.
- Averaging Principle: The measured value of a thermodynamic property f of a system in thermodynamic equilibrium is the ensemble average $\langle f \rangle$ of an ensemble in statistical equilibrium.
- Gibbs entropy (property of a Gibbs distribution ρ):

$$S_G(\rho) = -k\int_\Omega \rho(x,t)\log(\rho(x,t))\,dx$$

- How to pick a ρ: Require ρ be stationary and $S_G(\rho)$ be maximal.

Comments on Gibbs

- *Why ensembles?* "In an ensemble, recurrence and reverse behavior are no problem because it can be accepted that some systems in the ensemble will behave non-thermodynamically, provided that their contribution to the properties of the ensemble as a whole is taken into account when calculating ensemble averages." (Frigg 2008)
- *Statistical equilibrium*: Applies to an ensemble, and not a single system. A system in an ensemble in statistical equilibrium can be vastly out of thermodynamic equilibrium.
- *Gibbs entropy*: Applies to an ensemble, and not a single system. A system in an ensemble characterized by a maximal Gibbs entropy can be vastly out of thermodynamic equilibrium.