Topological pressure, free energy, equilibrium states and all that

Hugo Touchette

School of Mathematical Sciences, Queen Mary, University of London

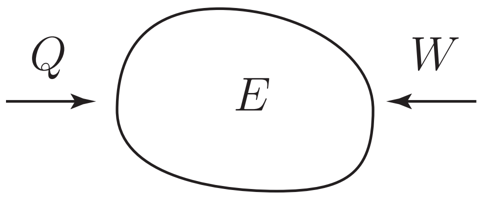
November 7, 2006

Outline

What is thermodynamics?

- Science of heat
  - how heat is transformed, stored, converted
  - how heat flows
  - science of heat engines (and fridges)
  - based on thermodynamics laws
- The actors:
  - Joule (1843) (units of energy)
  - Carnot (1824)
  - Kelvin (1850) (units of temperature)
  - Clausius (1850) (entropy = transformation energy)
- Was invented before atoms were discovered!
  - Heat = energy = caloric flow
  - Clear now that heat = kinetic energy

Thermodynamic potentials



- Energy: E
- Heat: Q
- Work: W
- Entropy: S
- Temperature: T

First law

$$\Delta E = \Delta Q + \Delta W$$

Second law

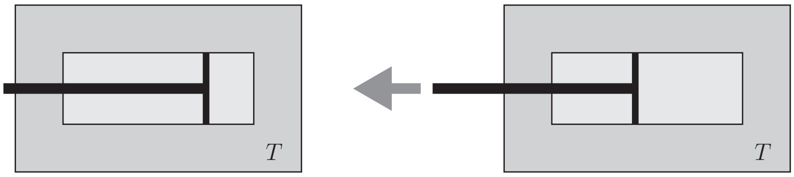
$$\Delta Q = T\ \Delta S$$

Free energy

$$F = E - TS$$

- Part of E which is *free* to be extracted when $T = constant$

$$\Delta F = -\Delta W$$



- Thermodynamic derivatives:

$$\left.\frac{\partial F}{\partial T}\right|_V = -S, \qquad \left.\frac{\partial F}{\partial V}\right|_T = -p$$

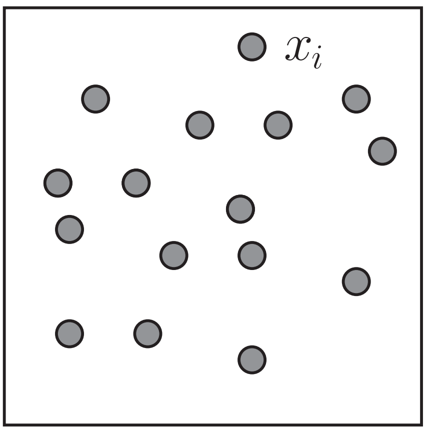
Gibbs's variational principle

The equilibrium state of a system has minimum free energy

Statistical mechanics (thermostatistics)

Derive the macroscopic from the microscopic

- Boltzmann (1872)
- Gibbs (1902)
- Maxwell, Planck, Einstein,...

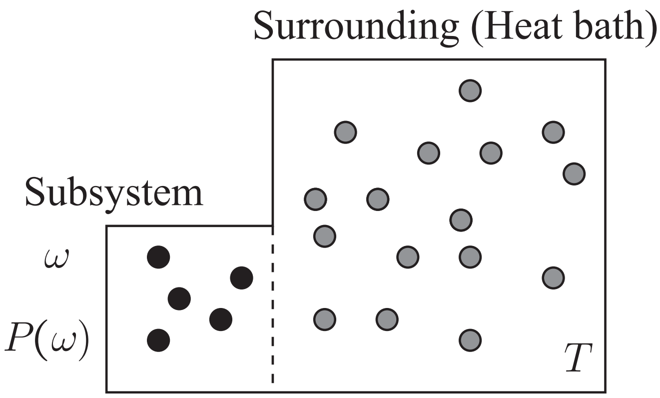


- State of one particle: x_i
- Energy of one particle: $u(x_i)$
- Microstate: $\omega = (x_1, x_2, \ldots, x_n)$
- Total energy:

$$U_N(\omega) = \sum_{i=1}^{N} u(x_i)$$

- $N \approx 10^{23}$ (Avogadro's number)

Introducing probabilities



- Canonical ensemble (Gibbs):

$$P(\omega) = \frac{e^{-\beta U_N(\omega)}}{Z_N(\beta)}$$

  - Inverse temperature: $\beta = (k_B T)^{-1}$
  - Partition function (*Zustandssumme*):

$$Z_N(\beta) = \sum_{\omega} e^{-\beta U_N(\omega)}$$

Equilibrium energy

- Equilibrium property:

$$u_N = \frac{U_N}{N} \stackrel{N\to\infty}{\longrightarrow} constant \qquad (i.p.)$$

- Probability for the mean energy:

$$P(u) = \sum_{\omega: U_N(\omega)=uN} P(\omega)$$

- Equilibrium energy:

$$u_\beta = global\ max\ of\ P(u)$$

Calculation of the equilibrium energy

- Entropy: $s(u)$

$$\#\ microstates\ with\ U_N = uN \approx e^{Ns(u)}$$

- Free energy:

$$\varphi(\beta) = -\lim_{N\to\infty} \frac{1}{N} \ln Z_N(\beta)$$

Variational principle

- u_β is the global min of $G_\beta(u) = \beta u - s(u)$
- $\varphi(\beta) = \inf_u\{\beta u - s(u)\}$ (Legendre transform)
- $\varphi'(\beta) = u_\beta$

Why free energy?

$$\varphi = \frac{u}{k_B T} - s, \qquad F = E - TS$$

Distribution of state

- Distribution of state:

$$\rho_N(x) = \frac{1}{N}\sum_{i=1}^{N} \delta(x_i - x) = \frac{\#\ particles\ with\ state\ x}{N}$$

  - Natural measure (dyn sys)
  - Empirical vector (large deviations)

- Energy:

$$\frac{U_N}{N} = \int \rho_N(x)\ u(x)\ dx = u(\rho_N)$$

- Equilibrium state:

$$\rho_\beta = global\ max\ of\ P(\rho_N)$$

Calculation of the equilibrium states

Variational principle

ρ_β is the global min of

$$G_\beta(\rho) = \beta u(\rho) - s(\rho) \qquad \textit{and} \qquad \varphi(\beta) = \beta u(\rho_\beta) - s(\rho_\beta)$$

- Statistical (Boltzmann-Gibbs-Shannon) entropy:

$$s(\rho) = -\int \rho(x) \ln \rho(x)\, dx$$

- Gibbs state:

$$\rho_\beta(x) = \frac{e^{-\beta u(x)}}{Z(\beta)}, \qquad Z(\beta) = \int e^{-\beta u(x)}\, dx$$

General approach

Consider a system of N particles

- Hamiltonian: $U_N(\omega)$
- Microstate: ω
- Macrostate: m
- Probability: $P_\beta(m)$
- Equilibrium state:

$$m_\beta = \textit{global max of } P_\beta(m)$$

- Meaning of equilibrium:

$$m \stackrel{N\to\infty}{\longrightarrow} m_\beta \qquad (i.p.)$$

- There is a variational principle behind m_β

Chaotic maps

- Map: $x_{n+1} = f(x_n)$ (smooth, expansive... nice enough)
- Trajectory: $\omega = (x_0, x_1, \ldots, x_{N-1})$
- Invariant measure: $\mu(x)$
- "Energy" function:

$$E_N(\omega) = E_N(x_0) = \frac{1}{N}\sum_{i=0}^{N-1} \phi(x_i)$$

  - Expansion coefficient:

$$E_N(x_0) = \frac{1}{N}\sum_{i=0}^{N-1} \ln|f'(x_i)|$$

  - Natural measure:

$$\rho_N(x_0) = \frac{1}{N}\sum_{i=0}^{N-1} \delta(x_i - x)$$

Equilibrium (thermodynamic) properties

- Lyapunov exponent:

$$E_N(x_0) = \frac{1}{N}\sum_{i=0}^{N-1} \ln|f'(x_i)| \stackrel{N\to\infty}{\longrightarrow} \lambda \qquad \mu - a.e.$$

- Sinai-Ruelle-Bowen (SRB) measure:

$$\rho_N(x_0) = \frac{1}{N}\sum_{i=0}^{N-1} \delta(x_i - x) \stackrel{N\to\infty}{\longrightarrow} \mu_{SRB} \qquad \mu - a.e.$$

Thermodynamic analogy (Ruelle, Sinai)

- Chaotic trajectories = random states of an N-particle system
- Concentration points = equilibrium states
- Variational principles behind equilibrium states

Thermodynamic formalism (naive)

- Energy function:

$$U_N(x_0) = \frac{1}{N} \sum_{i=0}^{N-1} \ln |f'(x_i)|$$

- Topological partition function:

$$Z_N(\beta) = \int dx_0 \ e^{-\beta N U_N(x_0)}$$

Why topological?

$$Z_N(\beta) = \int dx_0 \ e^{-\beta N U_N(x_0)}, \qquad Z_N(\beta) = \int d\mu(x_0) \ e^{-\beta N U_N(x_0)}$$

Counting and classifying trajectories

- Partition function:

$$Z_N(\beta) = \int du \ \Omega_N(u) e^{-\beta N u}$$

- Density of trajectories:

$$\Omega_N(u) = \# \ trajectories \ with \ U_N = u$$

- Entropy:

$$\Omega_N(u) \approx e^{Ns(u)}$$

- Topological pressure (free energy);

$$\varphi(\beta) = -\lim_{N\to\infty} \frac{1}{N} \ln Z_N(\beta)$$

Why pressure?

$$\left.\frac{\partial F}{\partial V}\right|_T = -p \qquad (pressure)$$

Connection between $\varphi(\beta)$ and $s(u)$

- Variational principle:

$$\varphi(\beta) = \inf_u \{\beta u - s(u)\}$$

- Inversion (under some conditions):

$$s(u) = \inf_\beta \{\beta u - \varphi(\beta)\}$$

- Lyapunov exponent:

$$\varphi(1) = 0, \qquad s(\lambda) = \lambda, \qquad \Omega_N(\lambda) \approx e^{N\lambda}, \qquad P(\omega) \approx e^{-N\lambda}$$

- These are the ideas – proving the results is another story!

Symbolic dynamics

- Map: $f : X \to X$ (expansive)
- Partition (coarse-graining): α
- Pre-images: $f^{-N}\alpha$
- Entropy:

$$H_N(\alpha, \mu) = -\sum_{A \in f^{-N}\alpha} \mu(A) \ln \mu(A)$$

- Mean entropy:

$$h(\alpha, \mu) = \lim_{N \to \infty} \frac{H_N(\alpha, \mu)}{N}$$

- Kolmogorov-Sinai entropy:

$$h(\mu) = \sup_\alpha h(\alpha, \mu)$$

Main results

- Variational principle for the pressure:

$$\varphi(\beta) = \inf_{\mu}\{\beta u(\mu) - h(\mu)\}, \qquad u(\mu) = \ln|f'(x)|$$

- Gibbs states:

$$\mu_\beta(x) = \frac{e^{-\beta u(x)}}{Z(\beta)}, \qquad Z(\beta) = \int dx\ e^{-\beta u(x)}$$

- Variational principle for SRB states:

$$\mu_{SRB} = \mu_{\beta=1}$$

- Kolmogorov-Sinai entropy:

$$\varphi(1) = 0 \Leftrightarrow h = \lambda$$

References

F. Reif
Fundamentals of Statistical and Thermal Physics
McGraw-Hill, 1965.

C. Beck and F. Schlögl
Thermodynamics of Chaotic Systems: An Introduction
Cambridge University Press, 1993.

D. Ruelle
Thermodynamic Formalism
Cambride University Press, 1978.

A. Katok and B. Hasselblatt
Introduction to the Modern Theory of Dynamical Systems
Cambridge University Press, 1995.

http://www.maths.qmul.ac.uk/˜ht
ht@maths.qmul.ac.uk