

Statistical Mechanics—a lightning course

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Canonical ensemble

- This tedious calculation demonstrates the clumsiness of the microcanonical ensemble, and explains why it is rarely used.
- It is also a somewhat artificial situation—a system in total thermal isolation.
- The *canonical ensemble* is appropriate for the description of a system in thermal equilibrium with a much larger system, e.g. a glass of water.
- So consider two systems described by Hamiltonians \mathcal{H}_1 and \mathcal{H}_2 of size N_1 and N_2 particles, occupying volumes V_1 and V_2 respectively, with $N_1 \ll N_2$.
- Consider first a microcanonical ensemble of the composite system, with total energy lying between E and $E + 2\delta E$.
- The two energies E_1 and E_2 must satisfy

$$E < E_1 + E_2 < E + 2\delta E.$$

Canonical ensemble

- The volume of Γ -space occupied by the composite system is $\Gamma_1(E_1)\Gamma_2(E_2)$, summed over all values of E_1 and E_2 .
- So

$$\Gamma(E) = \sum_{i=1}^{E/\delta E} \Gamma_1(E_i)\Gamma_2(E - E_i)$$

and E_i is the energy at the centre of each energy interval.

- The entropy of the composite system of $N = N_1 + N_2$ particles in a volume $V = V_1 + V_2$ is

$$S(E, V) = k \log \sum_{i=1}^{E/\delta E} \Gamma_1(E_i)\Gamma_2(E - E_i).$$

- Now let the largest term in the sum be $\Gamma_1(\bar{E}_1)\Gamma_2(\bar{E}_2)$, then

$$\Gamma_1(\bar{E}_1)\Gamma_2(\bar{E}_2) \leq \Gamma(E) \leq \frac{E}{\delta E} \Gamma_1(\bar{E}_1)\Gamma_2(\bar{E}_2),$$

or

$$k \log[\Gamma_1(\bar{E}_1)\Gamma_2(\bar{E}_2)] \leq S(E, V) \leq k \log[\Gamma_1(\bar{E}_1)\Gamma_2(\bar{E}_2)] + k \log \frac{E}{\delta E}.$$

- Now, as the number of particles in both systems is large, we expect that $\log \Gamma_{1,2} \propto N_{1,2}$ and $E \propto N_1 + N_2$.
- The term $k \log \frac{E}{\delta E}$ can be neglected as δE is independent of N . so we get

$$S(E, V) = S_1(\bar{E}_1, v_1) + S_2(\bar{E}_2, V_2) + O(\log N)$$

which proves the extensive property of the entropy, alluded to above, and, further, implies that the energies of the subsystems have the definite values \bar{E}_1 and \bar{E}_2 .

Canonical ensemble—continued

- So in our canonical ensemble, we have $\bar{E}_2 \gg \bar{E}_1$, and if we let $\Gamma_2(E_2)$ be the volume occupied by system 2 in its own Γ space, then the probability of finding system 1 in a state within $dp_1 dq_1$ of (p_1, q_1) , regardless of the state of system 2, is proportional to $dp_1 dq_1 \Gamma_2(E_2)$, where $E_2 = E - E_1$.
- Thus, up to a multiplicative constant, the density in Γ space for system 1 is

$$\rho(p_1, q_1) \propto \Gamma_2(E - E_1).$$

- Expanding around \bar{E}_1 , we have

$$k \log \Gamma_2(E - E_1) = S_2(E - E_1) = S_2(E) - E_1 \left(\frac{\partial S_2(E_2)}{\partial E_2} \right)_{E_2=E} + \dots$$

Canonical ensemble—continued

- So

$$k \log \Gamma_2(E - E_1) \approx S_2(E) - \frac{E_1}{T}$$

where T is the temperature of the larger subsystem.

- Hence

$$\Gamma_2(E - E_1) \approx \exp\left(\frac{S_2(E)}{k}\right) \exp\left(-\frac{E_1}{kT}\right).$$

- The first factor is independent of E_1 and is a constant from the point of view of the small subsystem.
- Now $E_1 = \mathcal{H}_1(p_1, q_1)$, we have (up to a multiplicative constant)

$$\rho(p, q) = e^{-\mathcal{H}(p, q)/kT}$$

where we have dropped the subscript 1, since we can forget about the larger subsystem, apart from the fact that its temperature is T .

Canonical ensemble—continued

- This ensemble, called the canonical ensemble, is appropriate for a system whose temperature is determined through contact with a heat reservoir.
- The volume in Γ -space occupied by the canonical ensemble is called the (canonical) partition function,

$$Z_N(V, T) \equiv \int \frac{d^{3N}p \, d^{3N}q}{N! h^{3N}} e^{-\beta \mathcal{H}(p, q)},$$

where $\beta = 1/kT$.

- The factor h^{3N} is for dimensional correction, while $N!$ accounts for “correct Boltzmann counting” as discussed above.
- Strictly speaking we should restrict the range of integration, but for large systems $\mathcal{H}(p, q)$ is dominated by a single value that lies within the allowed range of integration.

Canonical ensemble—continued

- Thermodynamics is obtained by the identity

$$Z_N(V, T) = e^{-\beta A(V, T)},$$

where $A(V, T)$ is the Helmholtz free-energy.

- This is justified by showing that (a) A is extensive, which follows from the factorisation of the partition function of a system made up of two sub-systems, and (b) A is related to U and S by $A = U - TS$.
- To prove this, rewrite it as $\langle \mathcal{H} \rangle = A - T \left(\frac{\partial A}{\partial T} \right)_V$, and note the identity

$$\int \frac{d^{3N}p \, d^{3N}q}{N! h^{3N}} e^{\beta[A(V, T) - \mathcal{H}(p, q)]} = 1.$$

- Differentiating w.r.t. β gives the required result.

Canonical ensemble—continued

- All other thermodynamic variables may be found by appropriate differentiation. Hence it is often said that statistical mechanics starts and ends with the calculation of the partition function.
- In algebraic combinatorics, we are frequently dealing with discrete systems.
- Then the definition of the partition function involves a sum over all configurations, rather than an integral, viz:

$$Z = \sum_{\text{all configurations}} e^{-\beta\mathcal{H}}.$$

Canonical ensemble—ideal gas equation of state

- Example: Calculate the equation of state of an ideal gas.
- We start as above with $\mathcal{H} = \frac{1}{2m} \sum_{i=1}^N p_i^2$.
- Then the partition function is

$$\begin{aligned} Z_N(V, T) &\equiv \int \frac{d^{3N}p \, d^{3N}q}{N! h^{3N}} e^{-\beta \mathcal{H}(p, q)} \\ &= \frac{V^N}{N! h^{3N}} \int d^{3N}p e^{-\beta/2m \sum p_i^2}. \end{aligned}$$

- We don't even need to calculate the integral, though it is easy. To refer to it in the future, let's call it λ^N .
- Since $A(V, T) = -\frac{1}{\beta} \log Z$, and $P = -\left(\frac{\partial A}{\partial V}\right)_T$, the only term we need is the term V^N , so we immediately obtain $PV = NkT$.

Canonical ensemble—ideal gas equation of state

- In going from the microcanonical to the canonical ensemble we relaxed the rather artificial restriction of an isolated system.
- In reality though we can never exactly specify the number of particles in a large system. All we know is some sort of average or approximation.
- This motivates the grand canonical ensemble, in which systems can have any number of particles, determined by external conditions.
- Just as we derived the density function in Γ -space of the canonical ensemble by considering the microcanonical ensemble, we will derive the grand canonical density function from the canonical one.

Grand Canonical Ensemble

- To find $\rho(p, q, N)$ in the GCE, consider the CE for a system of N particles, with volume V at temperature T .
- Focus on a small (but still macroscopic) sub-volume V_1 .
- The density $\rho(p_1, q_1, N_1)$ is proportional to the probability that in sub-volume V_1 there are N_1 particles with coordinates (p_1, q_1) .
- Let $N_2 = N - N_1$ and $V_2 = V - V_1$, and $N_2 \gg N_1$, $V_2 \gg V_1$.
- Neglecting interactions between V_2 and V_1 , we must have

$$\rho(p_1, q_1, N_1) \propto e^{-\beta\mathcal{H}(p_1, q_1, N_1)} \int_{V_2} dp_2 dq_2 e^{-\beta\mathcal{H}(p_2, q_2, N_2)}$$

where the integral extends over all p_2 , but only those values of q_2 which keep N_2 particles in the volume V_2 .

Grand Canonical Ensemble—continued

- It turns out to be convenient to choose the constant of proportionality so that

$$\rho(p_1, q_1, N_1) = \frac{N! e^{-\beta \mathcal{H}(p_1, q_1, N_1)} \int_{V_2} dp_2 dq_2 e^{-\beta \mathcal{H}(p_2, q_2, N_2)}}{N_1! N_2! \int_V dp dq e^{-\beta \mathcal{H}(p, q, N)}},$$

- or

$$\rho(p_1, q_1, N_1) = \frac{Z_{N_2}(V_2, T) e^{-\beta \mathcal{H}(p_1, q_1, N_1)}}{Z_N(V, T) N_1! h^{3N_1}}.$$

- Now

$$\frac{Z_{N_2}(V_2, T)}{Z_N(V, T)} = e^{-\beta[A(N_2, V_2, T) - A(N, V, T)]} = e^{-\beta[A(N - N_1, V - V_1, T) - A(N, V, T)]}$$

where A is the Helmholtz free energy introduced above.

Grand Canonical Ensemble—continued

- Since $N \gg N_1$ and $V \gg V_1$ we can write

$$\begin{aligned} & A(N - N_1, V - V_1, T) - A(N, V, T) \approx \\ & -N_1 \left(\frac{\partial A(N_2, V, T)}{\partial N_2} \right)_{N_2=N} - V_1 \left(\frac{\partial A(N, V_2, T)}{\partial V_2} \right)_{V_2=V} \\ & = -N_1 \mu + V_1 P, \end{aligned}$$

where μ is called the *chemical potential* and P is the (external) pressure.

- If we call $z = e^{\beta\mu}$ the *fugacity*, we have

$$\rho(p, q, N) = \frac{z^N}{N! h^{3N}} e^{-\beta PV - \beta \mathcal{H}(p, q)}. \quad (1)$$

- We can drop the subscript 1 as the external system can now be forgotten, except that it has temperature T , pressure P , and chemical potential μ .

Grand Canonical Ensemble—continued

- Defining now the *grand partition function* as

$$Q(z, V, T) \equiv \sum_{N=0}^{\infty} z^N Z_N(V, T),$$

then integrating both sides of eqn (??) over all p and q with N fixed, and summing N from 0 to ∞ , we find

$$\frac{PV}{kT} = \log Q(z, V, T).$$

- So the GPF gives P as a function of z , V , and T .
- The average number of particles is found from

$$N = z \frac{\partial}{\partial z} \log Q(z, V, T),$$

Grand Canonical Ensemble—continued

- The equation of state is found by eliminating z between the two equations above.
- All other thermodynamic functions may be obtained from the internal energy,

$$U = -\frac{\partial}{\partial \beta} \log Q(z, V, T),$$

or from the Helmholtz free-energy:

$$A = NkT \log z - kT \log Q(z, V, T).$$

- Whether using U or A , it is necessary to eliminate z in order to obtain U or A as a function of N , V and T .

Grand Canonical Ensemble—Ideal gas equation of state

- Example: The equation of state of an ideal gas follows from the expression $Z = \frac{V^N \lambda^N}{N! h^{3N}}$, where λ is the value of an integral we can evaluate, but needn't. Thus

$$Q(z, V, T) = e^{zV\lambda/h^3},$$

and

$$N = \frac{zV\lambda}{h^3} = PV/kT,$$

in agreement with the result obtained previously.

The Lenz-Ising model

- In 1920 Lenz proposed a microscopic theory of a ferromagnetic domain comprised of elementary spin dipoles constrained in quantized directions.
- He then gave it to his student Ernst Ising to work out the details. Ising did so, and in 1925 published his solution for a one-dimensional version of the model.
- It exhibited no ferromagnetic phase transition.
- Ising then incorrectly speculated that this conclusion would persist in higher dimensions.
- As this contradicted experimental observations, interest in the model died out, and models like those of Heisenberg, which was fully quantum-mechanical, and itinerant electron models of Bloch and others were considered necessary.

The Lenz-Ising model—continued

- The Lenz-Ising model was saved from obscurity by its application as a model of a binary alloy, when the calculations of Bethe, involving larger clusters of molecules) justified the Bragg-Williams mean-field theory.
- The model (as a model of a ferromagnet) assumes that “spins” may be up or down.
- Thus at each of N sites we have $s_j = \pm 1$.
- Each spin interacts with its nearest neighbour only, and (possibly) with an external magnetic field H .
- Thus the Hamiltonian is

$$\mathcal{H} = -J \sum_{\text{nearest neighbours}} s_i s_j - H \sum_{i=1}^N s_i.$$

- J is the coupling constant, and has units of energy.

The Lenz-Ising model—continued

- The simplest assumption is that both J and H are constant, but they can be site-dependent.
- For ferromagnetism we require $J > 0$, as this energetically favours aligned configurations. (For $J < 0$ we have anti-ferromagnetism.)
- If there are N spins, then the partition function involves the sum over all 2^N configurations (each spin independently $+1$ or -1).
- Consider a 1-dimensional chain, with spins numbered from 1 to N in zero magnetic field, ($H = 0$).

The Lenz-Ising model—continued

- Then

$$\begin{aligned} Z(N, T) &= \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \cdots \sum_{s_N=\pm 1} e^{\beta J \sum_{i=1}^{N-1} s_i s_{i+1}} \\ &= \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \cdots \sum_{s_N=\pm 1} \prod_{i=1}^{N-1} e^{\beta J s_i s_{i+1}}, \end{aligned}$$

where $\beta = 1/kT$.

- Consider the sum $\sum_{s_N=\pm 1}$. It applies only to the term $e^{\beta J s_{N-1} s_N}$, giving $2 \cosh \beta J s_{N-1} = 2 \cosh(\beta J)$ since the cosh function is an even function, and $s_i = \pm 1$.
- Thus $Z(N, T) = 2 \cosh(\beta J) \times Z(N-1, T)$, and $Z(1, T) = 2$, so

$$Z(N, T) = 2^N (\cosh \beta J)^{N-1}.$$

The Lenz-Ising model—continued

- The Helmholtz free-energy per particle is given by

$$-\beta A(T) = \lim_{N \rightarrow \infty} 1/N \log Z_N = \log(2 \cosh \beta J).$$

- The internal energy

$$U = -kT^2 \frac{\partial \beta A}{\partial T} = J \tanh \beta J.$$

- The specific heat

$$C_V = \frac{\partial U}{\partial T} = -J^2 / kT^2 \operatorname{sech}^2 \beta J.$$

- This is a smooth function of temperature for all $T > 0$, though it is sometimes used as evidence of a zero-temperature phase transition.

The Lenz-Ising model—continued

- We now consider the same model with cyclic boundary conditions, so that $s_{N+1} = s_1$.
- We will also include the external magnetic field, so that we can calculate other thermodynamic quantities, such as the magnetisation $M(H, T) = \frac{\partial A}{\partial H}$ and the susceptibility $\chi(H, T) = \frac{\partial M}{\partial H}$.
- In fact we are usually interested in the zero-field limit $H \rightarrow 0^+$, in which case we have the spontaneous magnetisation and the zero-field susceptibility, respectively.

The Lenz-Ising model—continued

- The partition function is now

$$\begin{aligned} Z(N, T) &= \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \cdots \sum_{s_N=\pm 1} e^{\beta \sum_{i=1}^N [Js_i s_{i+1} + Hs_i]} \\ &= \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \cdots \sum_{s_N=\pm 1} e^{\beta \sum_{i=1}^N [Js_i s_{i+1} + \frac{1}{2}H(s_i + s_{i+1})]}. \end{aligned}$$

which symmetrises the summand.

- Now define the 2×2 matrix P with elements

$$a_{i,j} = e^{\beta [Js_i s_j + \frac{1}{2}H(s_i + s_j)]}.$$

Thus

$$P = \begin{pmatrix} e^{\beta(J+H)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-H)} \end{pmatrix}$$

The Lenz-Ising model—continued

- In terms of P we may write the partition function

$$\begin{aligned} Z(N, T) &= \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \cdots \sum_{s_N=\pm 1} \langle s_1 | P | s_2 \rangle \langle s_2 | P | s_3 \rangle \cdots \langle s_N | P | s_1 \rangle \\ &= \sum_{s_1=\pm 1} \langle s_1 | P^N | s_1 \rangle = \text{Trace} P^N = \lambda_1^N + \lambda_2^N. \end{aligned}$$

- Exercise: Show that

$$\lambda_{1,2} = e^{\beta J} [\cosh(\beta H) \pm \sqrt{\sinh^2(\beta H) + e^{-4\beta J}}].$$

- So for $H = 0$ the largest eigenvalue is $2 \cosh(\beta J)$, in agreement with the case worked above.

The Lenz-Ising model—continued

- As $N \rightarrow \infty$ only the larger eigenvalue is relevant, and the Helmholtz free energy per spin is

$$-\beta A(T) = \lim_{N \rightarrow \infty} 1/N \log Z_N = \beta J + \log[\cosh(\beta H) + \sqrt{\cosh^2(\beta H) - 2e^{-2\beta J} \sinh^2(2\beta J)}].$$

- The magnetisation per spin is

$$M(H, T) = \frac{\sinh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}},$$

and so the spontaneous magnetisation, $M(0, T)$ vanishes for all $T > 0$.

Exercise: Calculate the susceptibility, $\chi = \frac{\partial M}{\partial H}$, and show that, in zero-field ($H = 0$) there is no singularity for $T > 0$.