

## 4.10: Appendix I- Additional Examples

### Three state system

Consider a spin-1 particle where  $\sigma = -1, 0, +1$ . We model this with the single particle Hamiltonian

$$\hat{h} = -\mu_0 H \sigma + \Delta(1 - \sigma^2). \quad (4.10.1)$$

We can also interpret this as describing a spin if  $\sigma = \pm 1$  and a vacancy if  $\sigma = 0$ . The parameter  $\Delta$  then represents the vacancy formation energy. The single particle partition function is

$$\zeta = \text{Tr } e^{-\beta \hat{h}} = e^{-\beta \Delta} + 2 \cosh(\beta \mu_0 H). \quad (4.10.2)$$

With  $N_S$  distinguishable noninteracting spins (at different sites in a crystalline lattice), we have  $Z = \zeta^{N_S}$  and

$$F \equiv N_S f = -k_B T \ln Z = -N_S k_B T \ln [e^{-\beta \Delta} + 2 \cosh(\beta \mu_0 H)], \quad (4.10.3)$$

where  $f = -k_B T \ln \zeta$  is the free energy of a single particle. Note that

$$\begin{aligned} \hat{n}_V &= 1 - \sigma^2 = \frac{\partial \hat{h}}{\partial \Delta} \\ \hat{m} &= \mu_0 \sigma = -\frac{\partial \hat{h}}{\partial H} \end{aligned}$$

are the vacancy number and magnetization, respectively. Thus,

$$n_V = \langle \hat{n}_V \rangle = \frac{\partial f}{\partial \Delta} = \frac{e^{-\Delta/k_B T}}{e^{-\Delta/k_B T} + 2 \cosh(\mu_0 H/k_B T)} \quad (4.10.4)$$

and

$$m = \langle \hat{m} \rangle = -\frac{\partial f}{\partial H} = \frac{2\mu_0 \sinh(\mu_0 H/k_B T)}{e^{-\Delta/k_B T} + 2 \cosh(\mu_0 H/k_B T)}. \quad (4.10.5)$$

At weak fields we can compute

$$\chi_T = \left. \frac{\partial m}{\partial H} \right|_{H=0} = \frac{\mu_0^2}{k_B T} \cdot \frac{2}{2 + e^{-\Delta/k_B T}}. \quad (4.10.6)$$

We thus obtain a modified Curie law. At temperatures  $T \ll \Delta/k_B$ , the vacancies are frozen out and we recover the usual Curie behavior. At high temperatures, where  $T \gg \Delta/k_B$ , the low temperature result is reduced by a factor of  $\frac{2}{3}$ , which accounts for the fact that one third of the time the particle is in a nonmagnetic state with  $\sigma = 0$ .

### Spins and vacancies on a surface

A collection of spin- $\frac{1}{2}$  particles is confined to a surface with  $N$  sites. For each site, let  $\sigma = 0$  if there is a vacancy,  $\sigma = +1$  if there is particle present with spin up, and  $\sigma = -1$  if there is a particle present with spin down. The particles are non-interacting, and the energy for each site is given by  $\varepsilon = -W\sigma^2$ , where  $-W < 0$  is the binding energy.

- Let  $Q = N_\uparrow + N_\downarrow$  be the number of spins, and  $N_0$  be the number of vacancies. The surface magnetization is  $M = N_\uparrow - N_\downarrow$ . Compute, in the microcanonical ensemble, the statistical entropy  $S(Q, M)$ .
- Let  $q = Q/N$  and  $m = M/N$  be the dimensionless particle density and magnetization density, respectively. Assuming that we are in the thermodynamic limit, where  $N$ ,  $Q$ , and  $M$  all tend to infinity, but with  $q$  and  $m$  finite, Find the temperature  $T(q, m)$ . Recall Stirling's formula

$$\ln(N!) = N \ln N - N + \mathcal{O}(\ln N). \quad (4.10.7)$$

- Show explicitly that  $T$  can be negative for this system. What does negative  $T$  mean? What physical degrees of freedom have been left out that would avoid this strange property?

There is a constraint on  $N_\uparrow$ ,  $N_0$ , and  $N_\downarrow$ :

$$N_\uparrow + N_0 + N_\downarrow = Q + N_0 = N. \quad (4.10.8)$$

The total energy of the system is  $E = -WQ$ .

- The number of states available to the system is

$$\Omega = \frac{N!}{N_{\uparrow}! N_0! N_{\downarrow}!} . \quad (4.10.9)$$

Fixing  $Q$  and  $M$ , along with the above constraint, is enough to completely determine  $\{N_{\uparrow}, N_0, N_{\downarrow}\}$ :

$$N_{\uparrow} = \frac{1}{2}(Q + M) \quad , \quad N_0 = N - Q \quad , \quad N_{\downarrow} = \frac{1}{2}(Q - M) , \quad (4.10.10)$$

whence

$$\Omega(Q, M) = \frac{N!}{[\frac{1}{2}(Q + M)]! [\frac{1}{2}(Q - M)]! (N - Q)!} . \quad (4.10.11)$$

The statistical entropy is  $S = k_B \ln \Omega$ :

$$S(Q, M) = k_B \ln(N!) - k_B \ln \left[ \frac{1}{2}(Q + M)! \right] - k_B \ln \left[ \frac{1}{2}(Q - M)! \right] - k_B \ln [(N - Q)!] . \quad (4.10.12)$$

- Now we invoke Stirling's rule,

$$\ln(N!) = N \ln N - N + \mathcal{O}(\ln N) , \quad (4.10.13)$$

to obtain

$$\begin{aligned} \ln \Omega(Q, M) &= N \ln N - N - \frac{1}{2}(Q + M) \ln \left[ \frac{1}{2}(Q + M) \right] + \frac{1}{2}(Q + M) \\ &\quad - \frac{1}{2}(Q - M) \ln \left[ \frac{1}{2}(Q - M) \right] + \frac{1}{2}(Q - M) \\ &\quad - (N - Q) \ln(N - Q) + (N - Q) \\ &= N \ln N - \frac{1}{2}Q \ln \left[ \frac{1}{4}(Q^2 - M^2) \right] - \frac{1}{2}M \ln \left( \frac{Q + M}{Q - M} \right) \end{aligned}$$

Combining terms,

$$\ln \Omega(Q, M) = -Nq \ln \left[ \frac{1}{2} \sqrt{q^2 - m^2} \right] - \frac{1}{2}Nm \ln \left( \frac{q+m}{q-m} \right) - N(1-q) \ln(1-q) , \quad (4.10.14)$$

where  $Q = Nq$  and  $M = Nm$ . Note that the entropy  $S = k_B \ln \Omega$  is extensive. The statistical entropy per site is thus

$$s(q, m) = -k_B q \ln \left[ \frac{1}{2} \sqrt{q^2 - m^2} \right] - \frac{1}{2}k_B m \ln \left( \frac{q+m}{q-m} \right) - k_B (1-q) \ln(1-q) . \quad (4.10.15)$$

The temperature is obtained from the relation

$$\begin{aligned} \frac{1}{T} &= \left( \frac{\partial S}{\partial E} \right)_M = \frac{1}{W} \left( \frac{\partial s}{\partial q} \right)_m \\ &= \frac{1}{W} \ln(1-q) - \frac{1}{W} \ln \left[ \frac{1}{2} \sqrt{q^2 - m^2} \right] . \end{aligned}$$

Thus,

$$T = \frac{W/k_B}{\ln[2(1-q)/\sqrt{q^2 - m^2}]} . \quad (4.10.16)$$

- We have  $0 \leq q \leq 1$  and  $-q \leq m \leq q$ , so  $T$  is real (thank heavens!). But it is easy to choose  $\{q, m\}$  such that  $T < 0$ . For example, when  $m = 0$  we have  $T = W/k_B \ln(2q^{-1} - 2)$  and  $T < 0$  for all  $q \in (\frac{2}{3}, 1]$ . The reason for this strange state of affairs is that the entropy  $S$  is bounded, and is not a monotonically increasing function of the energy  $E$  (or the dimensionless quantity  $Q$ ). The entropy is maximized for  $N_{\uparrow} = N_0 = N_{\downarrow} = \frac{1}{3}$ , which says  $m = 0$  and  $q = \frac{2}{3}$ . Increasing  $q$  beyond this point (with  $m = 0$  fixed) starts to reduce the entropy, and hence  $(\partial S / \partial E) < 0$  in this range, which immediately gives  $T < 0$ . What we've left out are kinetic degrees of freedom, such as vibrations and rotations, whose energies are unbounded, and which result in an increasing  $S(E)$  function.

## Fluctuating Interface

Consider an interface between two dissimilar fluids. In equilibrium, in a uniform gravitational field, the denser fluid is on the bottom. Let  $z = z(x, y)$  be the height the interface between the fluids, relative to equilibrium. The potential energy is a sum of gravitational and surface tension terms, with

$$U_{grav} = \int d^2x \int_0^z dz' \Delta \rho g z'$$

$$U_{surf} = \int d^2x \frac{1}{2} \sigma (\nabla z)^2.$$

We won't need the kinetic energy in our calculations, but we can include it just for completeness. It isn't so clear how to model it *a priori* so we will assume a rather general form

$$T = \int d^2x \int d^2x' \frac{1}{2} \mu(\mathbf{x}, \mathbf{x}') \frac{\partial z(\mathbf{x}, t)}{\partial t} \frac{\partial z(\mathbf{x}', t)}{\partial t}. \quad (4.10.17)$$

We assume that the  $(x, y)$  plane is a rectangle of dimensions  $L_x \times L_y$ . We also assume  $\mu(\mathbf{x}, \mathbf{x}') = \mu(|\mathbf{x} - \mathbf{x}'|)$ . We can then Fourier transform

$$z(\mathbf{x}) = (L_x L_y)^{-1/2} \sum_{\mathbf{k}} z_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{x}}, \quad (4.10.18)$$

where the wavevectors  $\mathbf{k}$  are quantized according to

$$\mathbf{k} = \frac{2\pi n_x}{L_x} \hat{\mathbf{x}} + \frac{2\pi n_y}{L_y} \hat{\mathbf{y}}, \quad (4.10.19)$$

with integer  $n_x$  and  $n_y$ , if we impose periodic boundary conditions (for calculational convenience). The Lagrangian is then

$$L = \frac{1}{2} \sum_{\mathbf{k}} \left[ \mu_{\mathbf{k}} |\dot{z}_{\mathbf{k}}|^2 - (g \Delta \rho + \sigma \mathbf{k}^2) |z_{\mathbf{k}}|^2 \right], \quad (4.10.20)$$

where

$$\mu_{\mathbf{k}} = \int d^2x \mu(|\mathbf{x}|) e^{-i\mathbf{k} \cdot \mathbf{x}}. \quad (4.10.21)$$

Since  $z(\mathbf{x}, t)$  is real, we have the relation  $z_{-\mathbf{k}} = z_{\mathbf{k}}^*$ , therefore the Fourier coefficients at  $\mathbf{k}$  and  $-\mathbf{k}$  are not independent. The canonical momenta are given by

$$p_{\mathbf{k}} = \frac{\partial L}{\partial \dot{z}_{\mathbf{k}}^*} = \mu_{\mathbf{k}} \dot{z}_{\mathbf{k}} \quad , \quad p_{\mathbf{k}}^* = \frac{\partial L}{\partial \dot{z}_{\mathbf{k}}} = \mu_{\mathbf{k}} \dot{z}_{\mathbf{k}}^* \quad (4.10.22)$$

The Hamiltonian is then

$$\begin{aligned} \hat{H} &= \sum'_{\mathbf{k}} \left[ p_{\mathbf{k}} z_{\mathbf{k}}^* + p_{\mathbf{k}}^* z_{\mathbf{k}} \right] - L \\ &= \sum'_{\mathbf{k}} \left[ \frac{|p_{\mathbf{k}}|^2}{\mu_{\mathbf{k}}} + (g \Delta \rho + \sigma \mathbf{k}^2) |z_{\mathbf{k}}|^2 \right], \end{aligned}$$

where the prime on the  $\mathbf{k}$  sum indicates that only one of the pair  $\{\mathbf{k}, -\mathbf{k}\}$  is to be included, for each  $\mathbf{k}$ .

We may now compute the ordinary canonical partition function:

$$\begin{aligned} Z &= \prod'_{\mathbf{k}} \int \frac{d^2 p_{\mathbf{k}} d^2 z_{\mathbf{k}}}{(2\pi \hbar)^2} e^{-|p_{\mathbf{k}}|^2 / \mu_{\mathbf{k}} k_B T} e^{-(g \Delta \rho + \sigma \mathbf{k}^2) |z_{\mathbf{k}}|^2 / k_B T} \\ &= \prod'_{\mathbf{k}} \left( \frac{k_B T}{2\hbar} \right)^2 \left( \frac{\mu_{\mathbf{k}}}{g \Delta \rho + \sigma \mathbf{k}^2} \right). \end{aligned}$$

Thus,

$$F = -k_B T \sum_{\mathbf{k}} \ln \left( \frac{k_B T}{2\hbar \Omega_{\mathbf{k}}} \right), \quad (4.10.23)$$

where<sup>13</sup>

$$\Omega_{\mathbf{k}} = \left( \frac{g \Delta \rho + \sigma \mathbf{k}^2}{\mu_{\mathbf{k}}} \right)^{1/2}. \quad (4.10.24)$$

is the normal mode frequency for surface oscillations at wavevector  $\mathbf{k}$ . For deep water waves, it is appropriate to take  $\mu_{\mathbf{k}} = \Delta \rho / |\mathbf{k}|$ , where  $\Delta \rho = \rho_L - \rho_G \approx \rho_L$  is the difference between the densities of water and air.

It is now easy to compute the thermal average

$$\begin{aligned} \langle |z_{\mathbf{k}}|^2 \rangle &= \int d^2 z_{\mathbf{k}} |z_{\mathbf{k}}|^2 e^{-(g \Delta \rho + \sigma \mathbf{k}^2) |z_{\mathbf{k}}|^2 / k_B T} / \int d^2 z_{\mathbf{k}} e^{-(g \Delta \rho + \sigma \mathbf{k}^2) |z_{\mathbf{k}}|^2 / k_B T} \\ &= \frac{k_B T}{g \Delta \rho + \sigma \mathbf{k}^2}. \end{aligned}$$

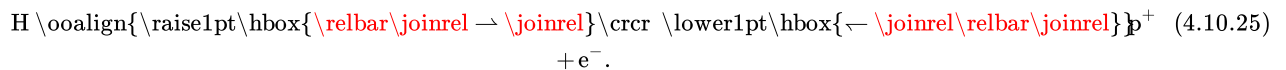
Note that this result does not depend on  $\mu_{\mathbf{k}}$ , on our choice of kinetic energy. One defines the *correlation function*

$$\begin{aligned} C(\mathbf{x}) \equiv \langle z(\mathbf{x}) z(0) \rangle &= \frac{1}{L_x L_y} \sum_{\mathbf{k}} \langle |z_{\mathbf{k}}|^2 \rangle e^{i\mathbf{k} \cdot \mathbf{x}} = \int \frac{d^2 k}{(2\pi)^2} \left( \frac{k_B T}{g \Delta \rho + \sigma \mathbf{k}^2} \right) e^{i\mathbf{k} \cdot \mathbf{x}} \\ &= \frac{k_B T}{4\pi\sigma} \int_0^\infty dq \frac{e^{i|q|\mathbf{x}|}}{\sqrt{q^2 + \xi^2}} = \frac{k_B T}{4\pi\sigma} K_0(|\mathbf{x}|/\xi), \end{aligned}$$

where  $\xi = \sqrt{g \Delta \rho / \sigma}$  is the correlation length, and where  $K_0(z)$  is the Bessel function of imaginary argument. The asymptotic behavior of  $K_0(z)$  for small  $z$  is  $K_0(z) \sim \ln(2/z)$ , whereas for large  $z$  one has  $K_0(z) \sim (\pi/2z)^{1/2} e^{-z}$ . We see that on large length scales the correlations decay exponentially, but on small length scales they diverge. This divergence is due to the improper energetics we have assigned to short wavelength fluctuations of the interface. Roughly, it can be cured by imposing a cutoff on the integral, or by insisting that the shortest distance scale is a molecular diameter.

## Dissociation of Molecular Hydrogen

Consider the reaction



In equilibrium, we have

$$\mu_H = \mu_p + \mu_e. \quad (4.10.26)$$

What is the relationship between the temperature  $T$  and the fraction  $x$  of hydrogen which is dissociated?

Let us assume a fraction  $x$  of the hydrogen is dissociated. Then the densities of H, p, and e are then

$$n_H = (1-x)n, \quad n_p = xn, \quad n_e = xn. \quad (4.10.27)$$

The single particle partition function for each species is

$$\zeta = \frac{g^N}{N!} \left( \frac{V}{\lambda_T^3} \right)^N e^{-N\varepsilon_{int}/k_B T}, \quad (4.10.28)$$

where  $g$  is the degeneracy and  $\varepsilon_{int}$  the internal energy for a given species. We have  $\varepsilon_{int} = 0$  for p and e, and  $\varepsilon_{int} = -\Delta$  for H, where  $\Delta = e^2/2a_B = 13.6$  eV, the binding energy of hydrogen. Neglecting hyperfine splittings<sup>14</sup>, we have  $g_H = 4$ , while  $g_e = g_p = 2$  because each has spin  $S = \frac{1}{2}$ . Thus, the associated grand potentials are

$$\begin{aligned} \Omega_H &= -g_H V k_B T \lambda_{T,H}^{-3} e^{(\mu_H + \Delta)/k_B T} \\ \Omega_p &= -g_p V k_B T \lambda_{T,p}^{-3} e^{\mu_p/k_B T} \\ \Omega_e &= -g_e V k_B T \lambda_{T,e}^{-3} e^{\mu_e/k_B T}, \end{aligned}$$

where

$$\lambda_{T,a} = \sqrt{\frac{2\pi\hbar^2}{m_a k_B T}} \quad (4.10.29)$$

for species  $a$ . The corresponding number densities are

$$n = \frac{1}{V} \left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V} = g \lambda_T^{-3} e^{(\mu - \varepsilon_{int})/k_B T}, \quad (4.10.30)$$

and the fugacity  $z = e^{\mu/k_B T}$  of a given species is given by

$$z = g^{-1} n \lambda_T^3 e^{\varepsilon_{int}/k_B T}. \quad (4.10.31)$$

We now invoke  $\mu_H = \mu_p + \mu_e$ , which says  $z_H = z_p z_e$ , or

$$g_H^{-1} n_H \lambda_{T,H}^3 e^{-\Delta/k_B T} = (g_p^{-1} n_p \lambda_{T,p}^3) (g_e^{-1} n_e \lambda_{T,e}^3), \quad (4.10.32)$$

which yields

$$\left( \frac{x^2}{1-x} \right) n \tilde{\lambda}_T^3 = e^{-\Delta/k_B T}, \quad (4.10.33)$$

where  $\tilde{\lambda}_T = \sqrt{2\pi\hbar^2/m^*k_B T}$ , with  $m^* = m_p m_e / m_H \approx m_e$ . Note that

$$\tilde{\lambda}_T = a_B \sqrt{\frac{4\pi m_H}{m_p}} \sqrt{\frac{\Delta}{k_B T}}, \quad (4.10.34)$$

where  $a_B = 0.529 \text{ \AA}$  is the Bohr radius. Thus, we have

$$\left( \frac{x^2}{1-x} \right) \cdot (4\pi)^{3/2} \nu = \left( \frac{T}{T_0} \right)^{3/2} e^{-T_0/T}, \quad (4.10.35)$$

where  $T_0 = \Delta/k_B = 1.578 \times 10^5 \text{ K}$  and  $\nu = n a_B^3$ . Consider for example a temperature  $T = 3000 \text{ K}$ , for which  $T_0/T = 52.6$ , and assume that  $x = \frac{1}{2}$ . We then find  $\nu = 1.69 \times 10^{-27}$ , corresponding to a density of  $n = 1.14 \times 10^{-2} \text{ cm}^{-3}$ . At this temperature, the fraction of hydrogen molecules in their first excited (2s) state is  $x' \sim e^{-T_0/2T} = 3.8 \times 10^{-12}$ . This is quite striking: half the hydrogen atoms are completely dissociated, which requires an energy of  $\Delta$ , yet the number in their first excited state, requiring energy  $\frac{1}{2}\Delta$ , is twelve orders of magnitude smaller. The student should reflect on why this can be the case.

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