

1a — The one-site partition function is:

$$Q_1 = 1 + e^{-\beta\epsilon}.$$

All the sites are independent, so this is the only partition function that really matters. The probabilities are then

$$p_0 = \frac{1}{1 + e^{-\beta\epsilon}}, \quad p_\epsilon = \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}.$$

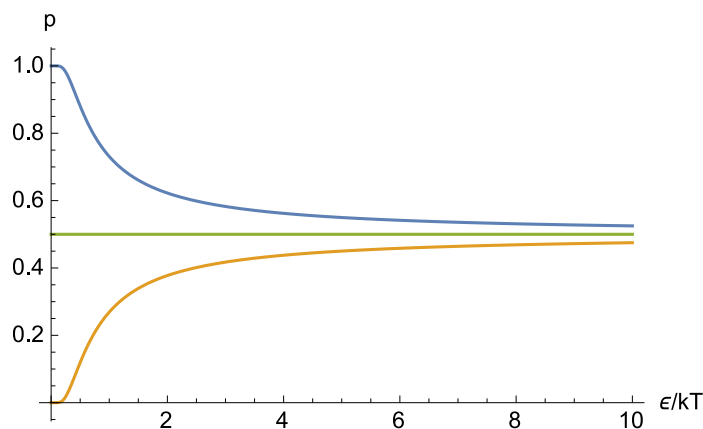


Figure 1: The blue curve is the probability of occupying the ground state, the yellow curve is the probability of occupying the excited state. The line $p = 1/2$ is drawn for reference.

1b — At $T = 0$, there is no energy in the system and there should be 0 systems in the excited state (and all in the ground state). At infinite temperature, each state is equally likely, so the probabilities limit to $1/2$ for both states.

1c — There are ω states that have energy 0, now, so the partition function is

$$Q_1 = 1 + 1 + 1 \dots + 1 + e^{-\beta\epsilon} = \omega + e^{-\beta\epsilon}.$$

The probability of having energy 0 or energy ϵ is

$$p_0 = \frac{\omega}{\omega + e^{-\beta\epsilon}}, \quad p_\epsilon = \frac{e^{-\beta\epsilon}}{\omega + e^{-\beta\epsilon}}.$$

1d — At $T = 0$, all of the systems should be in one of the ω ground states, and none in the excited state. As $T \rightarrow \infty$, we see that $e^{-\beta\epsilon} \rightarrow 1$, and

$$p_0(T = \infty) = \frac{\omega}{\omega + 1}, \quad p_\epsilon(T = \infty) = \frac{1}{1 + \omega}.$$

1e — The easiest way to see that the entropy is nonzero is to consider how many states each system has available at $T = 0$. The systems can only explore their ground states, of which they have ω , so the entropy is

$$S = k_B \log \omega.$$

Or we can take

$$\frac{S}{k_B} = \frac{\langle E \rangle - A}{k_B T}.$$

$$\frac{S}{k_B} = -\beta \frac{\partial \log Q_1}{\partial \beta} + \log Q_1.$$

$$\frac{S}{k_B} = \frac{\beta \varepsilon e^{-\beta \varepsilon}}{\omega + e^{-\beta \varepsilon}} + \log (\omega + e^{-\beta \varepsilon}).$$

As $\beta \rightarrow \infty$, the first term vanishes, and the second term just becomes $\log \omega$.

$$S \rightarrow k_B \log \omega.$$

2a — This problem doesn't require a Maxwell relation, just the cyclic identity:

$$\left. \frac{\partial X}{\partial Y} \right|_Z \left. \frac{\partial Y}{\partial Z} \right|_X \left. \frac{\partial Z}{\partial X} \right|_Y = -1.$$

Here, we want a relation with T , B , and S :

$$\left. \frac{\partial S}{\partial B} \right|_T \left. \frac{\partial B}{\partial T} \right|_S \left. \frac{\partial T}{\partial S} \right|_B = -1.$$

$$\left(\left. \frac{\partial S}{\partial B} \right|_T \right) \left(\left. \frac{\partial B}{\partial T} \right|_S \right) \left(\frac{T}{C_B} \right) = -1.$$

$$\left. \frac{\partial T}{\partial B} \right|_S = -\frac{T}{C_B} \left. \frac{\partial S}{\partial B} \right|_T > 0.$$

2b — We can use the result from part a and a Maxwell relation.

$$\left. \frac{\partial S}{\partial B} \right|_T = \left. \frac{\partial M}{\partial T} \right|_B.$$

So we have

$$\left. \frac{\partial T}{\partial B} \right|_S = -\frac{T}{C_B} \left. \frac{\partial M}{\partial T} \right|_B.$$

We can get $\frac{\partial M}{\partial T}\Big|_B$ from the equation of state. Taking a derivative with respect to temperature:

$$Mk_B + k_B T \frac{\partial M}{\partial T}\Big|_B = N \frac{\partial B}{\partial T}\Big|_B + J \frac{\partial M}{\partial T}\Big|_B.$$

The term $\frac{\partial B}{\partial T}\Big|_B = 0$, because we're holding B constant, of course. So, rearranging, we have

$$\frac{\partial M}{\partial T}\Big|_B = \frac{-Mk_B}{k_B T - J}.$$

If we plug in $M = NB/(k_B T - J)$,

$$\frac{\partial M}{\partial T}\Big|_B = \frac{-Nk_B B}{(k_B T - J)^2}.$$

Plugging this back in to $\frac{\partial T}{\partial B}\Big|_S$,

$$\frac{\partial T}{\partial B}\Big|_S = \frac{Nk_B T B}{(k_B T - J)^2 C_B}.$$

This is positive unless $k_B T = J$, where it is actually undefined. This equation of state is actually the equation of state of a ferromagnet in the limit of small B and small M . J is the strength of the coupling between magnetic moments, and when this energy becomes close to the order of $k_B T$, the system switches from one phase (paramagnetic) to another phase (ferromagnetic). This is similar to the phase transition in the Van der Waals equation that we'll be studying later.

3a — At constant E , V , and N , this is the microcanonical ensemble, where all available microstates are equally likely, so we have

$$p = \frac{1}{\Omega(E, V, N)}.$$

3b — The canonical partition function is defined as

$$Q(N, V, T) = \sum_{\nu(N, V, E)} e^{-\beta E_{\nu(N, V, E)}}.$$

Here, the sum over ν is restricted to microstates that have a constant volume, particle number, and energy. We can write this more naturally as

$$Q(N, V, T) = \sum_E \Omega(E, V, N) e^{-\beta E}.$$

This still sums over all the states of constant energy, volume, and particle number, but we're explicitly writing that we're summing over energies, not microstates, so we must include a factor

that counts how many microstates have energy E . The probability of observing a microstate with energy E is

$$p_{\nu(E)} = \frac{e^{-\beta E}}{Q(N, V, T)}.$$

The probability of observing **any** microstate whose energy is E , that is, the probability of observing that the system has energy E is

$$p_E = \frac{\Omega(N, V, E)e^{-\beta E}}{Q(N, V, T)}.$$

I accepted both answers, because the difference is very subtle.

3c — We can write the grand canonical partition function as

$$\Xi(\mu, V, T) = \sum_N \sum_E \Omega(E, V, N)e^{-\beta E + \beta N\mu} = \sum_N Q(N, V, T)e^{\beta N\mu}.$$

The probability of observing a microstate with energy E and particle number N is

$$p_{\nu(E, N)} = \frac{e^{-\beta E + \beta N\mu}}{\Xi(\mu, V, T)}.$$

The probability of observing **any** microstate with energy E and particle number N , that is, the probability of observing that the system has energy E and particle number N is

$$p_{E, N} = \frac{\Omega(E, N, V)e^{-\beta E + \beta N\mu}}{\Xi(\mu, V, T)}.$$

Once again, I accepted either answer.

3d — To transform from the constant-shape ensemble to the constant-chemical potential ensemble, we perform a transformation that should look exactly like the grand canonical ensemble transformation, because α and $d\sigma$ have the same role as μ and dN in the thermodynamic relation $dE = TdS - PdV + \mu dN + \alpha d\sigma$.

$$\Theta(T, V, N, \alpha) = \sum_{\sigma} Q(T, V, N, \sigma)e^{\beta\alpha\sigma}.$$

What this means is that we have to somehow specify the shape of our particles by some variable σ , then we have to find a way to sum over all possible values of σ . For example, for simplicity, we could look at two dimensions. The unit circle is defined by

$$1 = x^2 + y^2.$$

A diamond shape whose corners are $(\pm 1, 0)$ and $(0, \pm 1)$ can be defined by

$$1 = |x| + |y|.$$

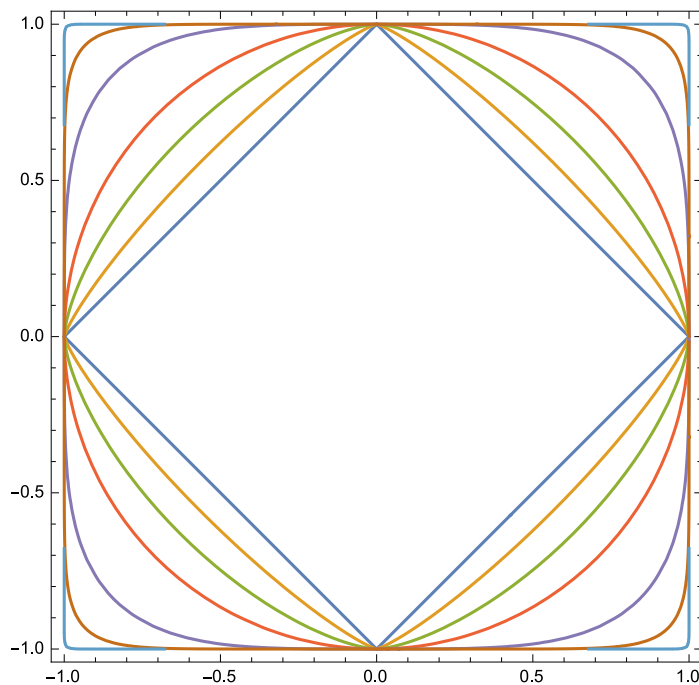


Figure 2: The plot $1 = |x|^\sigma + |y|^\sigma$ plotted for $\sigma = 1, 1.2, 1.5, 2, 4, 10, 100$. As $\sigma \rightarrow \infty$, we have a square.

If we let

$$1 = |x|^\sigma + |y|^\sigma,$$

we can ramp σ from 1 to 2 to go continuously from a diamond to a circle. This is just an example of how we might perform a summation like this: if we allow σ to take discrete values, we'd sum over those discrete values, and if it were continuous, we'd do an integration like we do when we do phase space integrals.

4a — The canonical partition function for one particle is

$$Q_1 = \frac{1}{h^2} \int d\mathbf{p} \int d\mathbf{r} e^{-\frac{\beta p^2}{2m} + \frac{1}{2}\beta m\omega^2 r^2}.$$

The momentum integral we've done many times, so we just pick up two factors of the thermal wavelength:

$$Q_1 = \frac{1}{\lambda^2} \int d\mathbf{r} e^{\frac{1}{2}\beta m\omega^2 r^2}.$$

Note that there is a positive sign in the exponent! This isn't a Gaussian integral, but it is actually very simple when we go to polar coordinates, the transformation of which was given on the back of the exam:

$$Q_1 = \frac{1}{\lambda^2} \int_0^{2\pi} d\theta \int_0^R r dr e^{\frac{1}{2}\beta m\omega^2 r^2}.$$

The angular integral gives 2π , and we can define $u = \frac{\beta m \omega^2}{2} r^2$:

$$Q_1 = \frac{2\pi}{\lambda^2 \beta m \omega^2} \int_0^{\frac{\beta m \omega^2 R^2}{2}} du e^u.$$

$$Q_1 = \frac{2\pi}{\lambda^2 \beta m \omega^2} \left(e^{\frac{\beta m \omega^2 R^2}{2}} - 1 \right).$$

We can substitute in the volume (area, really, we're in two dimensions) with $R^2 = V/\pi$:

$$Q_1 = \frac{2\pi}{\lambda^2 \beta m \omega^2} \left(e^{\frac{\beta m \omega^2 V}{2\pi}} - 1 \right).$$

The total partition function is of course $Q = Q_1^N / N!$.

4b — The energy is

$$E = -\frac{\partial \log Q}{\partial \beta} = -N \frac{\partial \log Q_1}{\partial \beta}.$$

$$E = N \frac{\partial}{\partial \beta} \left(2 \log \lambda + \log \beta - \log \left(e^{\frac{\beta m \omega^2 V}{2\pi}} - 1 \right) \right).$$

Remember $\lambda \propto \sqrt{\beta}$:

$$E = Nk_B T + Nk_B T - \frac{Nm\omega^2 V}{2\pi} \frac{e^{\frac{\beta m \omega^2 V}{2\pi}}}{e^{\frac{\beta m \omega^2 V}{2\pi}} - 1}.$$

$$E = Nk_B T + Nk_B T - \frac{Nm\omega^2 V}{2\pi} \frac{1}{1 - e^{-\frac{\beta m \omega^2 V}{2\pi}}}.$$

The first term $Nk_B T$ is the ideal gas term, which comes from equipartition. The second and third term are corrections. We can check that they will go away in $\omega \rightarrow 0$ limit:

$$E(\omega \rightarrow 0) \approx Nk_B T + Nk_B T - \frac{Nm\omega^2 V}{2\pi} \frac{1}{\frac{\beta m \omega^2 V}{2\pi}}.$$

$$E \approx Nk_B T.$$

4c — The pressure is very similar to the energy:

$$P = -\frac{\partial A}{\partial V} = Nk_B T \frac{\partial \log Q_1}{\partial V}.$$

$$P = Nk_B T \frac{\partial}{\partial V} \log \left(e^{\frac{\beta m \omega^2 V}{2\pi}} - 1 \right).$$

$$P = \frac{Nm\omega^2}{2\pi} \frac{1}{1 - e^{-\frac{\beta m \omega^2 V}{2\pi}}}.$$

In the limit of really high temperatures $\beta \rightarrow 0$,

$$P \rightarrow \frac{Nm\omega^2}{2\pi} \frac{1}{\frac{\beta m\omega^2 V}{2\pi}}.$$

$$P \rightarrow \frac{Nk_B T}{V}.$$

4d — The pressure at very *low* temperatures is more interesting. The exponential in the denominator goes to 0, and we get

$$P = \frac{Nm\omega^2}{2\pi}.$$

We can think of this from a totally mechanical perspective: at extremely low temperatures, the lowest energy state has all the particles pinned against the side of the container by the centrifugal force. This force is $F = m\omega^2 R$ per particle. The pressure is a force divided by an area (but here in two dimensions, we divided the force by a length), and the length here is $2\pi R$, the circumference of the container. There are N particles, so we have

$$P = \frac{NF}{2\pi R} = \frac{Nm\omega^2}{2\pi}.$$