From Kardar.

Problem 4.1 (Classical Harmonic Oscillator)**.** Consider N harmonic oscillators with coordinates and momenta $\{q_i, p_i\}$, and subject to a Hamiltonian

$$\mathcal{H}(\{q_i, p_i\}) = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + \frac{m\omega^2 q_i^2}{2}\right].$$

(a) Calculate the entropy S, as a function of the total energy E. (*Hint.* By appropriate change of scale, the surface of constant energy can be deformed into a sphere. You man then ignore the difference between the surface area and volume for $N \gg 1$. A more elegant method is to implement this deformation through a canonical transformation.)

(b) Calculate the energy E, and heat capacity C, as functions of temperature T, and N.

(c) Find the joint probability density $P(p, q)$ for a single oscillator. Hence calculate the mean kinetic energy, and mean potential energy for each oscillator.

Solution. (a) Simply make the transformation $p_i \mapsto P_i = p_i/\sqrt{m\omega}$ and $q_i \mapsto Q_i = \sqrt{m\omega} q_i$. It is clear that this transformation is canonical as $\{P_i, P_j\} = \{p_i, p_j\}/m\omega = 0$, $\{Q_i, Q_j\} = \{q_i, q_j\} m\omega = 0$, and

$$\{Q_i, P_j\} = \left\{\left(m\omega^2\right)^{1/4} q_i, \left(m\omega^2\right)^{-1/4} p_j\right\} = \{q_i, p_j\} = \delta_{ij}.$$

The Hamiltonian in terms of the new coordinates is

$$\mathcal{H}(\{Q_i, P_i\}) = \frac{\omega}{2} \sum_{i=1}^{N} \left[P_i^2 + Q_i^2\right].$$

Notice then that the constant energy surface defined by

$$E = \frac{\omega}{2} \sum_{i=1}^{N} \left[P_i^2 + Q_i^2\right]$$

is a sphere in $2N$ dimensional phase space with radius $\sqrt{2E/\omega}$. The surface area of the sphere is then given by

$$\Omega(E) = \frac{1}{h^N} \frac{2\pi^N}{(N-1)!} \left(\frac{2E}{\omega}\right)^{(2N-1)/2},$$

where we have divided by h^N to account for the units. For $N \gg 1$, this becomes

$$\Omega(E) \approx \left[\frac{\pi}{h} \left(\frac{e}{N}\right) \left(\frac{2E}{\omega}\right)\right]^N.$$

Note that since the transformation was canonical, the phase space volume is preserved, so this is also the volume for the energy surface in the original coordinates.

The entropy is then

$$\begin{aligned} S(E) &= k_B \ln \Omega(E) \\ &= N k_B \ln \left(\frac{2\pi e E}{N h \omega} \right). \end{aligned}$$

(b) The temperature is given by

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_N = \frac{N k_B}{E},$$

so

$$E = N k_B T.$$

The heat capacity is then

$$C = \frac{\partial E}{\partial T} = N k_B.$$

(c) For a single oscillator, the joint probability density is

$$\begin{aligned} P(p, q) &= \frac{\Omega(E - p^2/2m - m\omega^2 q^2/2, N-1)}{h\Omega(E, N)} \\ &= \frac{N\omega}{2\pi e E} \left[\left(\frac{N}{N-1} \right) \left(\frac{E - p^2/2m - m\omega^2 q^2/2}{E} \right) \right]^N \\ &\approx \frac{\omega}{2\pi k_B T} \exp \left[-\frac{p^2/2m + m\omega^2 q^2/2}{k_B T} \right], \end{aligned}$$

as for $N \gg 1$,

$$\left(\frac{N}{N-1} \right)^N \to e,$$

and with $E = N k_B T$,

$$\left(1 - \frac{p^2/m + m\omega^2 q^2}{2 N k_B T} \right)^N \to \exp \left[-\frac{p^2/2m + m\omega^2 q^2/2}{k_B T} \right].$$

Note then that the mean kinetic energy is given by

$$\begin{aligned}
\langle K \rangle &= \int \frac{p^2}{2m} \frac{\omega}{2\pi k_B T} \exp\left[-\frac{p^2/2m + m\omega^2 q^2/2}{k_B T} \right] dpdq \\
&= \frac{\omega}{2\pi k_B T} \int \exp\left[-\frac{m\omega^2 q^2}{2k_B T} \right] dq \int \frac{p^2}{2m} \exp\left[-\frac{p^2}{2mk_B T} \right] dp \\
&= \frac{\omega}{2\pi k_B T} \left(\frac{2\pi k_B T}{m\omega^2} \right)^{1/2} (2\pi m k_B T)^{1/2} \frac{k_B T}{2} \\
&= \frac{1}{2} k_B T,
\end{aligned}$$

where we have divided by h because of the measure $dpdq/h$.

The potential energy can then be found by

$$\langle U \rangle = \langle E \rangle - \langle K \rangle = k_B T - \frac{1}{2} k_B T = \frac{1}{2} k_B T,$$

where $E = N \langle E \rangle \implies \langle E \rangle = k_B T$. Note that these results are consistent with the equipartition theorem. □

Problem 4.3 (Relativistic particles)**.** N *indistinguishable* relativistic particles move in *one dimension* subject to a Hamiltonian

$$\mathcal{H}(\{p_i, q_i\}) = \sum_{i=1}^{N} \left[c\,|p_i| + U(q_i) \right],$$

with $U(q_i) = 0$ for $0 \le q_i \le L$, and $U(q_i) = \infty$ otherwise. Consider a *microcanonical* ensemble of total energy E.

(a) Compute the contribution of the coordinates q_i to the availale volume in phase space $\Omega(E, L, N)$.

(b) Compute the contribution of the momenta p_i to $\Omega(E, L, N)$. (*Hint.* The volume of the hyperpyramid defined by $\sum_{i=1}^{d} x_i \le R$, and $x_i \ge 0$, in d dimensions is $R^d/d!$).

(c) Compute the entropy $S(E, L, N)$.

(d) Calculate the one-dimensional pressure P.

(e) Obtain the heat capacities C_L and C_P.

(f) What is the probability $p(p_1)$ of finding a particle with momentum p_1?

Solution. (a) The contribution of the coordinates is simply the allowed volume, L^N, divided by $N!$ to account for indistinguishable particles, so in $L^N/N!$.

(b) The allowed momenta must be on the energy hypersurface defined by

$$\sum_{i=1}^{N} c\,|p_i| = E.$$

To get the volume of this hypersurface, notice that the volume of the region

$$\sum_{i=1}^{N} |p_i| \leq \frac{E}{c}$$

is given by $2^N (E/c)^N/N!$, with the 2^N factor accounting for the possible signs of p_i. Allowing for a small range of energies δE around E, we see that the volume within this range is

$$\frac{2^N}{c}\frac{(E/c)^{N-1}}{(N-1)!}\delta E.$$

However, this is not equal to the surface area times δE as δE is not increase the thickness normal to the surface but parallel to the axes. In fact, the thickness only increases by $\delta E/\sqrt{N}$ in the normal direction, so $\sqrt{N}\delta n = \delta E$, and the surface area is then

$$\frac{2^N\sqrt{N}}{c}\frac{(E/c)^{N-1}}{(N-1)!} = \frac{1}{E\sqrt{N}N!}\left(\frac{2E}{c}\right)^N.$$

Ignoring the difference between surface area and volume, this is the contribution of the momenta to Ω.

(c) The total phase space volume is then (accounting for the phase space measure with h^{-N})

$$\Omega = \frac{1}{E\sqrt{N}(N!)^2}\left(\frac{2LE}{hc}\right)^N.$$

The entropy is then

$$\begin{aligned}
S &= k_B \ln \Omega \\
&= k_B\left[N\ln\left(\frac{2LE}{hc}\right) - \frac{1}{2}\ln N - \ln E + 2N\ln\frac{e}{N} - \frac{1}{2}\ln 2\pi N\right] \\
&\approx Nk_B \ln\left(\frac{2e^2LE}{hcN^2}\right),
\end{aligned}$$

dropping all terms of order $\ln N$ and smaller.

(d) The pressure is given by

$$P = T\frac{\partial S}{\partial L}\bigg|_{E,N} = T\left(\frac{Nk_B}{L}\right) = \frac{Nk_BT}{L}.$$

(e) We can calculate

$$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_{L,N} = \frac{Nk_B}{E} \implies E = Nk_BT.$$

Then

$$C_L = \frac{\partial Q}{\partial T}\bigg|_L = \frac{\partial E}{\partial T}\bigg|_L = Nk_B.$$

Also,

$$C_P = \frac{\partial Q}{\partial T}\bigg|_P = \frac{\partial E}{\partial T}\bigg|_P + P\frac{\partial L}{\partial T}\bigg|_P = Nk_B + P\left(\frac{Nk_B}{P}\right) = 2Nk_B.$$

(f) The probability of finding a particle with momentum p_1 is given by

$$P(p_1) = \frac{\Omega_p(E - E_1, N-1)}{\Omega_p(E, N)},$$

where $E_1 = c\,|p_1|$ and Ω_p is the momentum contribution to the phase space volume. This is given by

$$\begin{aligned} P(p_1) &= \sqrt{\frac{N}{N-1}}N\left(\frac{c}{2E}\right)\left(\frac{E - c\,|p_1|}{E}\right)^{N-1} \\ &= \sqrt{\frac{N}{N-1}}N\left(\frac{c}{2Nk_BT}\right)\left(1 - \frac{c\,|p_1|}{Nk_BT}\right)^{N-1} \\ &\approx \frac{c}{2k_BT}\exp\left[-\frac{c\,|p_1|}{k_BT}\right] \end{aligned}$$

for $N \to \infty$ □

Problem 4.8 (Curie Susceptibility)**.** Consider N non-interacting quantized spins in a magnetic field $\mathbf{B} = B\hat{\mathbf{z}}$, and at a temperature T. The work done by the field is given by BM_z, with a magnetization of $M_z = \mu\sum_{i=1}^N m_i$. For each spin, m_i takes only the $2s+1$ values $-s, -s+1, \ldots, s-1, s$.

(a) Calculate the Gibbs partition function $\mathcal{Z}(T, B)$. (Note that the ensemble corresponding to the macrostate (T, B) includes magnetic work.)

(b) Calculate the Gibbs free energy $G(T, B)$, and show that for small B,

$$G(B) = G(0) - \frac{N\mu^2 s(s+1)B^2}{6k_BT} + \mathcal{O}(B^4).$$

(c) Calculate the zero field susceptibility $\chi = \partial M_z/\partial B|_{B=0}$, and show that it satisfies *Curie's law*

$$\chi = c/T.$$

(d) Show that $C_B - C_M = cB^2/T^2$, where C_B and C_M are heat capacities at constant B and M, respectively.

Solution. (a) The Gibbs partition function is given by

$$\mathcal{Z}(T,B) = \sum_{\{m_i\}} \exp\left[\beta B M_z\right] = \sum_{\{m_i\}} \prod_{i=1}^{N} e^{\beta B \mu m_i} = \left[\sum_{m_i=-s}^{s} e^{\beta B \mu m_i}\right]^N .$$

(b) The Gibbs free energy is then

$$G(T,B) = -k_B T \ln \mathcal{Z}(T,B) = -N k_B T \ln \left(\sum_{m_i=-s}^{s} e^{\beta B \mu m_i}\right).$$

For small B, we get that

$$G(B) = G(0) + \sum_{n=1}^{\infty} \frac{1}{n!} \frac{\partial^n G}{\partial B^n}\bigg|_{B=0} B^n.$$

The first derivative is given by

$$\frac{\partial G}{\partial B}\bigg|_{B=0} = -N k_B T \frac{\sum_{m=-s}^{s} \beta \mu m e^{\beta B \mu m}}{\sum_{m=-s}^{s} e^{\beta B \mu m}}\Bigg|_{B=0} = -N k_B T \frac{\beta \mu}{2s+1} \sum_{m=-s}^{s} m = 0,$$

as the terms in the sum cancel. It follows then that the second derivative is

$$\frac{\partial^2 G}{\partial B^2}\bigg|_{B=0} = -N k_B T \frac{\beta^2 \mu^2}{2s+1} \sum_{m=-s}^{s} m^2.$$

For integer s, the sum becomes

$$\sum_{m=-s}^{s} m^2 = 2 \sum_{m=1}^{s} m^2 = \frac{s(s+1)(2s+1)}{3}.$$

For half-integer s, the sum evaluates to the same expression, as can be seen inductively:

$$\sum_{m=-1/2}^{1/2} m^2 = \frac{1}{2} = \frac{(1/2)(1/2+1)(2(1/2)+1)}{3},$$

and

$$\frac{(s+1)((s+1)+1)(2(s+1)+1)}{3} = \frac{s(s+1)(2s+1)}{3} + 2(s+1)^2.$$

Thus,

$$\frac{\partial^2 G}{\partial B^2} = -\frac{N\mu^2 s(s+1)}{3k_BT},$$

so

$$G(B) = G_0 - \frac{N\mu^2 s(s+1)B^2}{6k_BT} + \mathcal{O}(B^4),$$

where the B^3 term vanishes because like the first order term, the sum involves only odd powers, so the terms of the sum cancel.

(c) First we calculate the average magnetization

$$\langle M_z \rangle = k_BT\frac{\partial \ln \mathcal{Z}}{\partial B} = -\frac{\partial G}{\partial B}.$$

Then

$$\chi = \left.\frac{\partial \langle M_z \rangle}{\partial B}\right|_{B=0} = -\left.\frac{\partial^2 G}{\partial B^2}\right|_{B=0} = \frac{N\mu^2 s(s+1)}{3k_BT} = \frac{c}{T},$$

where

$$c = \frac{N\mu^2 s(s+1)}{3k_B},$$

satisfying Curie's law.

(d) Since the work done is BdM, we get that

$$C_B - C_M = -B\left.\frac{\partial \langle M_z \rangle}{\partial T}\right|_B = B\frac{\partial^2 G}{\partial B \partial T}.$$

Differentiating first with respect to T, we get that

$$\begin{aligned}\frac{\partial G}{\partial T} &= -Nk_B \ln\left(\sum_{m=-s}^{s} e^{\beta B\mu m}\right) - Nk_BT\left[\frac{\sum_{m=-s}^{s} B\mu m e^{\beta B\mu m}}{\sum_{m=-s}^{s} e^{\beta B\mu m}}\right]\left(-\frac{1}{k_BT^2}\right) \\ &= \frac{G}{T} - \frac{B}{T}\frac{\partial G}{\partial B}.\end{aligned}$$

Then,

$$\begin{aligned}C_B - C_M &= \frac{B}{T}\frac{\partial}{\partial B}\left[G - B\frac{\partial G}{\partial B}\right] \\ &= \frac{B}{T}\left[\frac{\partial G}{\partial B} - \frac{\partial G}{\partial B} - B\frac{\partial^2 G}{\partial B^2}\right] \\ &= -\frac{B^2}{T}\frac{\partial^2 G}{\partial B^2} \\ &\approx \frac{B^2}{T}\chi \\ &= \frac{cB^2}{T^2}.\end{aligned}$$

□

Problem 4.12 (Polar rods)**.** Consider rod-shaped molecules with moment of inertia I, and a dipole moment μ. The contribution of the rotational degrees of freedom to the Hamiltonian is given by

$$\mathcal{H}_{\text{rot.}} = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) - \mu E\cos\theta,$$

where E is an external electric field. ($\phi \in [0, 2\pi]$, $\theta \in [0, \pi]$ are the azimuthal and polar angles, and p_ϕ, p_θ are their conjugate momenta.)

(a) Calculate the contribution of the rotational degrees of freedom of each dipole to the *classical* partition function.

(b) Obtain the mean polarization $P = \langle \mu\cos\theta\rangle$ of each dipole.

(c) Find the *zero-field* polarizability

$$\chi_T = \left.\frac{\partial P}{\partial E}\right|_{E=0}.$$

(d) Calculate the rotational energy per particle (at finite E), and comment on its high- and low-temperature limits.

(e) Sketch the rotational heat capacity per dipole.

Solution. (a) The contribution of the rotational degrees of freedom to the classical partition function is given by

$$\begin{aligned}
Z_{\text{rot.}} &= \int d\phi d\theta dp_\phi dp_\theta \exp\left[-\beta\mathcal{H}_{\text{rot.}}\right] \\
&= 2\pi\int_{-\infty}^{\infty} e^{-\beta p_\theta^2/2I}\,dp_\theta \int_0^\pi e^{\beta\mu E\cos\theta}\int_{-\infty}^{\infty} e^{-\beta p_\phi^2/2I\sin^2\theta}\,dp_\phi\,d\theta \\
&= 2\pi\sqrt{\frac{2\pi I}{\beta}}\int_0^\pi e^{\beta\mu E\cos\theta}\sin\theta\sqrt{\frac{2\pi I}{\beta}}\,d\theta \\
&= \frac{4\pi^2 I}{\beta}\int_{-1}^{1} e^{\beta\mu E y}\,dy \\
&= \frac{4\pi^2 I}{\beta^2\mu E}\left[e^{\beta\mu E} - e^{-\beta\mu E}\right] \\
&= \frac{8\pi^2 I}{\beta^2\mu E}\sinh(\beta\mu E).
\end{aligned}$$

(b) The mean polarization is given by

$$P = \langle\mu\cos\theta\rangle = \frac{1}{\beta}\frac{\partial}{\partial E}\ln Z_{\text{rot.}} = -\frac{1}{\beta E} + \mu\coth(\beta\mu E).$$

(c) The zero-field polarizability is

$$\chi_T = \frac{\partial P}{\partial E}\bigg|_{E=0} = \left(\frac{1}{\beta E^2} - \frac{\beta\mu^2}{\sinh^2(\beta\mu E)}\right)\bigg|_{E=0}.$$

For $x \ll 1$, we have

$$\operatorname{csch} x \approx \frac{1}{x} - \frac{x}{6} \implies \operatorname{csch}^2 x \approx \frac{1}{x^2} - \frac{1}{3},$$

so

$$\chi_T = \left(\frac{1}{\beta E^2} - \beta\mu^2\left(\frac{1}{(\beta\mu E)^2} - \frac{1}{3}\right)\right) = \frac{\beta\mu^2}{3}.$$

(d) The rotational energy per particle at finite E is given by

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = \frac{2}{\beta} - \mu E\coth(\beta\mu E).$$

In the high-temperature limit ($\beta \to 0$), we get that

$$\langle E\rangle \to \frac{2}{\beta} - \frac{\mu E}{\beta\mu E} = \frac{1}{\beta} = k_B T.$$

In the low-temperature limit ($\beta \to \infty$), we get that

$$\langle E\rangle \to 2k_B T - \mu E.$$

(e) The rotational heat capacity per dipole is given by

$$C = \frac{\partial\langle E\rangle}{\partial T} = 2k_B - \frac{(\mu E)^2}{k_B T^2}\operatorname{csch}^2\left(\frac{\mu E}{k_B T}\right).$$

For $T \to 0$, we get that $C \to 2k_B$. For $T \to \infty$, this becomes

$$C \to 2k_B - \frac{(\mu E)^2}{k_B T^2}\left(\frac{k_B T}{\mu E}\right)^2 = k_B.$$

This looks like

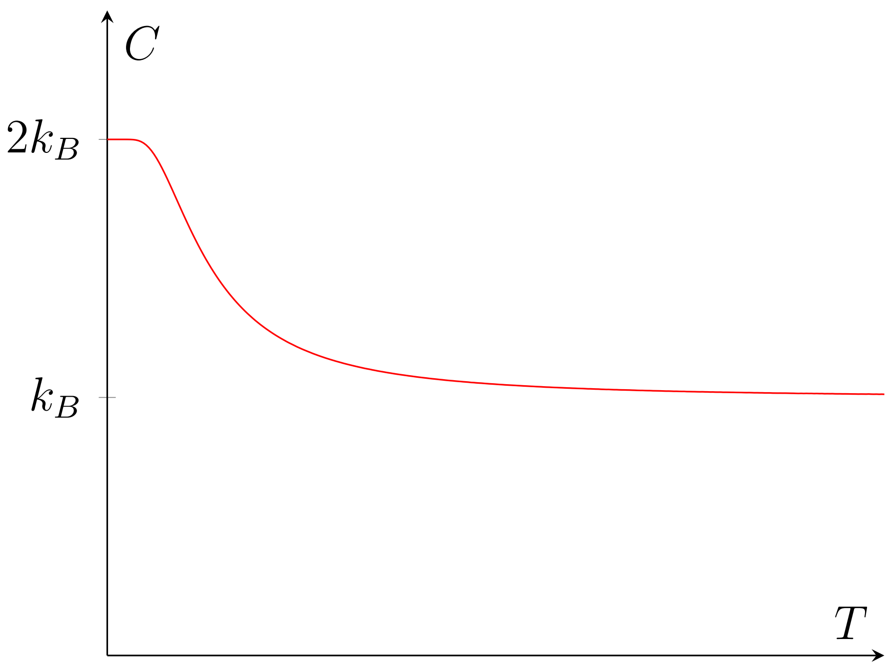

Figure 1: C vs T.

$\square$