

Exercise 3.1 Non-interacting Particles in the Gravitational Field

a) The canonical partition function Z is given by

$$Z(N, T) = \frac{1}{h^{3N} N!} \int d^{3N} q d^{3N} p e^{-\beta \mathcal{H}(p, q)}, \quad \beta = 1/k_B T. \quad (1)$$

With the Hamiltonian of the system

$$\mathcal{H}(p, q) = \sum_{i=1}^N \{p_i^2/2m + mgz_i\}$$

(note that we have set $\vec{q}_i = (x_i, y_i, z_i)$) one obtains

$$\begin{aligned} Z(N, T) &= \frac{1}{h^{3N} N!} \prod_{i=1}^N \int d^3 q_i d^3 p_i e^{-\beta(p_i^2/2m + mgz_i)} \\ &= \frac{1}{h^{3N} N!} \prod_{i=1}^N \pi R^2 \int_0^\infty dz_i e^{-\beta mgz_i} \int d^3 p_i e^{-\beta p_i^2/2m} \\ &= \frac{1}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^{3N/2} \left(\frac{\pi R^2}{\beta mg} \right)^N. \end{aligned} \quad (2)$$

This leads to the Helmholtz free energy

$$\begin{aligned} F(N, T) &= -k_B T \log Z(N, T) \\ &= -N k_B T \log \left[\left(\frac{2\pi m}{h^2} \right)^{3/2} \frac{\pi R^2}{mg} (k_B T)^{5/2} \right] + N k_B T \log N - N k_B T, \end{aligned} \quad (3)$$

using Stirling's approximation $\log N! \approx N \log N - N$. Consequently, one finds the following expression for the entropy,

$$\begin{aligned} S(N, T) &= - \left(\frac{\partial F}{\partial T} \right)_N \\ &= \frac{5}{2} N k_B + N k_B \log \left[\left(\frac{2\pi m}{h^2} \right)^{3/2} \frac{\pi R^2}{mg} (k_B T)^{5/2} \right] - N k_B \log N + N k_B. \end{aligned} \quad (4)$$

Finally, the internal energy is given by

$$U(N, T) = - \frac{\partial \log Z}{\partial \beta} = \frac{5}{2} N k_B T. \quad (5)$$

b) We first note that the local density for just one particle $\langle \delta(z_i - z) \rangle$ is independent of the phase-space coordinates of the other $N - 1$ particles and uniform in the planar coordinates, such that $\pi R^2 n(z) = N \langle \delta(z_i - z) \rangle$ for any i . We have

$$\begin{aligned} \langle \delta(z_i - z) \rangle &= \frac{1}{Z} \frac{1}{h^{3N} N!} \int d^{3N} \tilde{q} d^{3N} \tilde{p} \delta(z_i - z) e^{-\beta \mathcal{H}} \\ &= \frac{1}{\int dz_i e^{-\beta mgz_i}} e^{-\beta mgz} \\ &= \beta mg e^{-\beta mgz}, \end{aligned} \quad (6)$$

such that

$$n(z) = N \frac{\beta mg}{\pi R^2} e^{-\beta mgz}. \quad (7)$$

The local pressure $p(z)$ exerted by the particles above z is obtained by adding up the force $f(z) = -\nabla V_{\text{grav}}(z) = -mg$ and we find

$$p(z) = \frac{\int_{q_z > z} d^3q n(q_z) |f(q_z)|}{\pi R^2} = \frac{mg}{\pi R^2} \int dq_x dq_y \int_z^\infty dq_z n(q_z) = N \frac{mg}{\pi R^2} e^{-\beta mgz}. \quad (8)$$

Obviously, the (local) thermal equation of state holds,

$$p(z) = n(z) k_B T. \quad (9)$$

For the local energy density we find

$$\begin{aligned} u(z) &= \frac{N}{Z} \frac{1}{h^{3N} N!} \int d^{3(N-1)} \tilde{q} d^{3(N-1)} \tilde{p} \int d^3p d^3q \frac{\delta(q_z - z)}{\pi R^2} \left(\frac{p^2}{2m} + mgq_z \right) e^{-\beta \mathcal{H}} \\ &= \frac{N}{Z} \frac{Z}{\int d^3p d^3q e^{-\beta(p^2/2m + mgq_z)}} \int d^3p \left(\frac{p^2}{2m} + mgz \right) e^{-\beta(p^2/2m + mgz)} \end{aligned} \quad (10)$$

$$\begin{aligned} &= N \left(\frac{\beta}{2\pi m} \right)^{3/2} \frac{\beta mg}{\pi R^2} \int d^3p \left(\frac{p^2}{2m} + mgz \right) e^{-\beta(p^2/2m + mgz)} \\ &= N \frac{\beta mg}{\pi R^2} \left(\frac{3}{2} k_B T + mgz \right) e^{-\beta mgz}, \end{aligned} \quad (11)$$

such that $\int d^3q u(q_z) = U$. We find

$$u(z) = \left(\frac{3}{2} k_B T + mgz \right) n(z). \quad (12)$$

The first term corresponds to a local caloric equation of state while the second term is the potential energy.

- c) i) Using equation (4) we obtain

$$C = T \left(\frac{\partial S}{\partial T} \right)_N = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_N = \frac{5}{2} N k_B. \quad (13)$$

- ii) We first rewrite the Hamiltonian as

$$\mathcal{H}(p, q) = \sum_{i=1}^N \left\{ \left(\sum_{\mu} \frac{p_{i\mu}}{2} \frac{\partial \mathcal{H}}{\partial p_{i\mu}} \right) + z_i \frac{\partial \mathcal{H}}{\partial z_i} \right\}, \quad (14)$$

where i enumerates particles and μ runs over the coordinates. The equipartition law is given by

$$\left\langle q_{i\mu} \frac{\partial \mathcal{H}}{\partial q_{j\nu}} \right\rangle = \delta_{ij} \delta_{\mu\nu} k_B T = \left\langle p_{i\mu} \frac{\partial \mathcal{H}}{\partial p_{j\nu}} \right\rangle, \quad (15)$$

and with $U = \langle \mathcal{H} \rangle$ we find

$$\begin{aligned} C &= \frac{\partial \langle \mathcal{H} \rangle}{\partial T} = \frac{\partial}{\partial T} \sum_{i=1}^N \left\{ \frac{1}{2} \sum_{\mu} \left\langle p_{i\mu} \frac{\partial \mathcal{H}}{\partial p_{i\mu}} \right\rangle + \left\langle z_i \frac{\partial \mathcal{H}}{\partial z_i} \right\rangle \right\} \\ &= \frac{\partial}{\partial T} N \left\{ \frac{3}{2} k_B T + k_B T \right\} = \frac{3}{2} N k_B + N k_B. \end{aligned} \quad (16)$$

The final result is the same as in i), but we are now able to identify the different contributions: The first term stands for the kinetic contribution to the internal energy whereas the second term is due to the potential energy of the particles in the gravitational field.

- iii) Defining the specific volume via the local particle density, $v(z) = N/n(z)$, the thermal expansion coefficient takes the form

$$\begin{aligned}\alpha(z) &= \frac{1}{v(z)} \left(\frac{\partial v(z)}{\partial T} \right)_{p(z)} \\ &= \frac{-1}{n(z)} \left(\frac{\partial n(z)}{\partial T} \right)_{p(z)} \\ &= \frac{-1}{n(z)} \frac{-p(z)}{k_B T^2} = \frac{1}{T},\end{aligned}\tag{17}$$

where the thermal equation of state equation (9) has been used for the last step. With the relation given on the exercise sheet we thus find for the specific heat at constant pressure

$$c_p(z) = \frac{3}{2}n(z)k_B + n(z)k_B = c_V + n(z)k_B.\tag{18}$$

We see that a non-interacting particle ensemble subjected to an external force corresponds to the situation of an ideal gas with locally constant external pressure in a specific volume. We can only make a statement about local variables, while in a free ideal gas this relation holds globally. The C we calculated in i) and ii) can neither be identified with a C_p or a C_V but is a C_N .

- iv) If the particles are non-interacting and the potential energy only depends on the spatial coordinates,

$$\mathcal{H}(p, q) = \sum_{i=1}^N [\mathcal{H}_{\text{kin}}(p_i) + \mathcal{H}_{\text{pot}}(q_i)],$$

the evaluation of the variance of \mathcal{H} simplifies substantially,

$$\begin{aligned}(\Delta\mathcal{H})^2 &= \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \sum_{i,j=1}^N \left\{ \langle [\mathcal{H}_{\text{kin}}(p_i) + \mathcal{H}_{\text{pot}}(q_i)][\mathcal{H}_{\text{kin}}(p_j) + \mathcal{H}_{\text{pot}}(q_j)] \rangle \right. \\ &\quad \left. - \langle [\mathcal{H}_{\text{kin}}(p_i) + \mathcal{H}_{\text{pot}}(q_i)] \rangle \langle [\mathcal{H}_{\text{kin}}(p_j) + \mathcal{H}_{\text{pot}}(q_j)] \rangle \right\} \\ &= \sum_{i,j=1}^N \left\{ \langle \mathcal{H}_{\text{kin}}(p_i)\mathcal{H}_{\text{kin}}(p_j) \rangle + \langle \mathcal{H}_{\text{pot}}(q_i)\mathcal{H}_{\text{pot}}(q_j) \rangle \right. \\ &\quad \left. - \langle \mathcal{H}_{\text{kin}}(p_i) \rangle \langle \mathcal{H}_{\text{kin}}(p_j) \rangle - \langle \mathcal{H}_{\text{pot}}(q_i) \rangle \langle \mathcal{H}_{\text{pot}}(q_j) \rangle \right\} \\ &= (\Delta\mathcal{H}_{\text{kin}})^2 + (\Delta\mathcal{H}_{\text{pot}})^2.\end{aligned}\tag{19}$$

It follows directly that the heat capacity $C = (\Delta\mathcal{H})^2/k_B T^2$ separates in a similar fashion, $C = C_{\text{kin}} + C_{\text{pot}}$. The kinetic contribution is identical to the case of an ideal gas, and reads $C_{\text{kin}} = \frac{3}{2}Nk_B$.

The variance of the potential energy contribution is $(\Delta\mathcal{H}_{\text{pot}})^2 = N(mg)^2(\Delta z)^2$, since $\mathcal{H}_{\text{pot}}(q) = mgz$. The total potential energy is given by $Nmg\langle z \rangle$, where

$$\langle z \rangle = \frac{\pi R^2}{N} \int_0^\infty dz zn(z) = \frac{1}{\beta mg}\tag{20}$$

is the mean height of the particles. Derivation with respect to temperature gives

$$\begin{aligned}\frac{\partial}{\partial T}\langle z \rangle &= -k_B\beta^2 \{ \langle z \rangle \langle \mathcal{H}_{\text{pot}} \rangle - \langle \mathcal{H}_{\text{pot}} z \rangle \} = -k_B\beta^2 \{ \langle z \rangle mg \langle z \rangle - mg \langle z^2 \rangle \} \\ &= k_B\beta^2 mg (\Delta z)^2 = \frac{k_B\beta^2}{Nm g} (\Delta \mathcal{H}_{\text{pot}})^2 = \frac{C_{\text{pot}}}{Nm g},\end{aligned}\quad (21)$$

such that

$$\partial_T Nm g \langle z \rangle = C_{\text{pot}}.$$

The potential contribution to the heat capacity can thus be calculated in a similar fashion as $C = \partial_T U$ for the total potential energy $Nm g \langle z \rangle$. It follows directly that

$$C = C_{\text{kin}} + C_{\text{pot}} = \frac{3}{2} N k_B + N k_B, \quad (22)$$

as expected.

Exercise 3.2 Classical Ideal Paramagnet II

a) The partition function has the usual product form

$$Z = \prod_{i=1}^N \int d\Omega_i e^{\beta m H \cos \theta_i} = \left(2\pi \int_{-1}^1 d \cos \theta_i e^{\beta m H \cos \theta_i} \right)^N = \left(\frac{4\pi}{\beta m H} \sinh(\beta m H) \right)^N \equiv Z_m^N. \quad (23)$$

The link to thermodynamics is obtained via the Helmholtz free energy and the internal energy,

$$F(T, H, N) = -k_B T \log Z = N k_B T \log(\beta m H) - N k_B T \log(4\pi \sinh(\beta m H)), \quad (24)$$

$$U(T, H, N) = -\frac{\partial}{\partial \beta} \log Z = N k_B T - N m H \coth(\beta m H). \quad (25)$$

From this we directly obtain

$$C_H = \left(\frac{\partial U}{\partial T} \right)_H = N k_B - N k_B \left(\frac{m H}{k_B T \sinh(m H / k_B T)} \right)^2. \quad (26)$$

In the zero temperature limit we have

$$C_H \rightarrow N k_B, \quad \text{as } T \rightarrow 0, \quad (27)$$

which is non-vanishing. It corresponds to the contribution of the potential energy of a two-dimensional harmonic oscillator (the fluctuating magnetic moments nearly aligned with the magnetic field feel a harmonic potential).

b) Because the partition function has a product form, the magnetization can be written as

$$\langle \vec{m} \rangle = \frac{1}{Z_m} \int d\Omega \vec{m}(\phi, \theta) e^{\beta m H \cos \theta}, \quad (28)$$

leading to $\langle m_x \rangle = \langle m_y \rangle = 0$ and

$$\langle m_z \rangle = \frac{2\pi m}{Z_m} \int_{-1}^1 d \cos \theta \cos \theta e^{\beta m H \cos \theta} = m \coth \left(\frac{m H}{k_B T} \right) - \frac{k_B T}{H}. \quad (29)$$

It is clear from equation (24) that the above expression satisfies the usual thermodynamical relation.

b) The mean square magnetization $\langle m_z^2 \rangle$ can be obtained in a similar fashion

$$\langle m_z^2 \rangle = \frac{2\pi m}{Z_m} \int_{-1}^1 d \cos \theta \cos^2 \theta e^{\beta m H \cos \theta} = -\frac{2k_B T}{H} \left(m \coth(mH/k_B T) - \frac{k_B T}{H} \right) + m^2. \quad (30)$$

Deriving $\langle m_z \rangle$ with respect to H_z , we directly get the magnetic susceptibility

$$\chi_{zz} = - \left(\frac{\partial^2 F}{\partial H_z^2} \right)_{T,N} = \frac{Nm^2}{k_B T} \left[\left(\frac{k_B T}{mH} \right)^2 - \frac{1}{\sinh^2(mH/k_B T)} \right], \quad (31)$$

such that we finally obtain the fluctuation-dissipation relation

$$(\Delta m_z)^2 = \langle m_z^2 \rangle - \langle m_z \rangle^2 = \frac{k_B T}{N} \chi_{zz}. \quad (32)$$

We see that the fluctuations of the magnetization are connected to its response function, the magnetic susceptibility. This is a special case of the more general fluctuation-dissipation theorem.