Exercise 1. ***Planets as black bodies?***

The Stefan-Boltzmann law states that the emission power per unit surface area of a black body reads

$$P_{em} = \sigma T^4 \quad \text{with} \quad \sigma = \frac{\pi^2 k_B^4}{60\hbar^3 c^2} \approx 5.6704 \cdot 10^{-8}\ \mathrm{Js^{-1}m^{-2}K^{-4}}. \tag{1}$$

(a) Making use of the Stefan-Boltzmann law, estimate the temperature of the Earth, Mars and Venus as if they were black bodies.

Hint. Compute the emission power of the sun as if it were a black body and assume that the energy emitted and absorbed by each planet has to balance.

Solution. The Stefan-Boltzmann law gives a power per unit surface of emission. In order to estimate the temperature of the Earth as if it was a black body, we need to equate the energy emitted with the energy absorbed. The Earth absorbs the radiation from the Sun, therefore we need to calculate the amount of solar energy that reaches us. In order to calculate the total power emitted by the Sun we need to integrate equation (1) over the Sun's surface, i.e.,

$$P_S = P_{em} \cdot 4\pi R_S^2 = \sigma T_S^4 \cdot 4\pi R_S^2, \tag{S.1}$$

where T_S and R_S are the Sun surface temperature and radius, respectively. This power is spread spherically across space, and reaches the Earth after traveling the average distance a_0 (also called *astronomical unit*). Therefore, the power per unit surface reaching the Earth is

$$p_{abs} = \frac{P_S}{4\pi a_0^2} \approx 1.4 \cdot 10^3\,\mathrm{W}. \tag{S.2}$$

In order to obtain the total power absorbed by the Earth we finally need to multiply the quantity above with the cross section[1] of the Earth sphere, i.e,

$$P_{abs} = \frac{P_S}{4\pi a_0^2} \cdot \pi R_E^2 = \frac{P_S R_E^2}{4a_0^2} \tag{S.3}$$

where R_E is the Earth radius. The total power emitted by the Earth is again given by integrating equation (1) over the Earth surface,

$$P_E = P_{em} \cdot 4\pi R_E^2 = \sigma T_E^4 \cdot 4\pi R_E^2, \tag{S.4}$$

where T_E is the temperature we want to estimate. We thus equate the emitted and absorbed power to find

$$\sigma T_E^4 \cdot 4\pi R_E^2 = \frac{\sigma T_S^4 R_E^2 4\pi R_S^2}{4a_0^2} \Leftrightarrow T_E^4 = T_S^4 \frac{R_S^2}{4a_0^2} \Leftrightarrow T_E = T_S \sqrt{\frac{R_S}{2a_0}}, \tag{S.5}$$

which is independent of the Earth radius. Using for $T_S \approx 5778\,\mathrm{K}$, for $R_S \approx 6.96 \cdot 10^8\,\mathrm{m}$ and for $a_0 \approx 1.496 \cdot 10^{11}\mathrm{m}$ we obtain

$$T_E \approx T_S \cdot 1.525 \cdot 10^{-3/2} \approx 279\,\mathrm{K}. \tag{S.6}$$

The very same calculation applies in the cases of the other planets, and making use of $a_M = 1.524 a_0$ (average distance of Mars from the Sun) and $a_V = 0.7233 a_0$ (average distance of Venus from the Sun) we obtain:

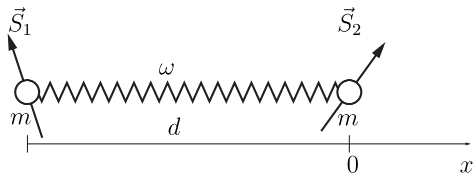
$$\begin{aligned} T_M &\approx T_S \cdot 1.236 \cdot 10^{-3/2} \approx 226\,\mathrm{K}, \\ T_V &\approx T_S \cdot 1.793 \cdot 10^{-3/2} \approx 328\,\mathrm{K}. \end{aligned} \tag{S.7}$$

(b) The correct results for the average temperatures are 288 K for the Earth, 218 K for Mars and 735 K for Venus. How do they compare with your estimates? What could be the reasons of the discrepancies?

[1] And *not* half of the surface of the Earth.

Solution. There are many approximations in the calculation but there are two main effects, one lowering and one increasing the real temperature. First, all planets have albedo, such that part of the incoming solar radiation is scattered without absorption. This effect reduces the absorbed power and therefore the temperature. On the other hand, planets have an atmosphere, such that both the incoming and the emitted radiation suffer from reflection. The exact effect of the atmosphere is very complicated. For the Earth it turns out that the amount of radiation emitted from the surface (which, due to the lower temperature, has a higher wavelength) suffers more from reflection than the incoming Sun's radiation (mainly in the visible range of the electromagnetic spectrum), such that the resulting temperature of the Earth is slightly higher than the black-body estimate. A similar reasoning is valid for the other planets, whose atmospheres are mainly composed of CO_2, with the important difference that the atmosphere of Mars is much thinner (therefore yielding a good estimate) while the one of Venus is much thicker (therefore yielding a bad estimate).

Exercise 2. ***Magnetostriction in a Spin-Dimer-Model.***



We consider a dimer consisting of two spin-1/2 particles with the Hamiltonian

$$\mathcal{H}_0 = J\left(\vec{S}_1 \cdot \vec{S}_2 + 3/4\right) ,$$

with $J > 0$. We already considered a dimer in exercise 4.2, but note that the energy levels are now shifted by a constant. This time, however, the distance between the two spins is not fixed and they are connected to each other by a spring. The spin–spin coupling constant depends on the distance between the two sites such that the Hamilton operator of the system is

$$\mathcal{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 + J(1-\lambda\hat{x})\left(\vec{S}_1 \cdot \vec{S}_2 + 3/4\right) , \tag{2}$$

where $\lambda \geq 0$, m is the mass of the two constituents, $m\omega^2$ is the spring constant, and x denotes the displacement from the equilibrium distance d between the two spins (defined for no spin-spin interaction).

(a) Calculate the canonical partition function, the internal energy, the specific heat and the entropy. Discuss the behavior of the entropy in the limit $T \to 0$ for different values of λ.

Hints. Rewrite the Hamiltonian using the total spin operator as in Exercise 4.2, and bring it by completing the square to the following form

$$\mathcal{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\,\hat{X}^2 + \tilde{J}\,\hat{n}_t , \tag{3}$$

where $\hat{n}_t \equiv \vec{S}^2/2$ is the projector on the triplet subspace, $\hat{X}$ and $\tilde{J}$ are appropriately shifted quantities of $\hat{x}$ and J ($\hat{X}$ may depend on $\hat{n}_t$), and we have set $\hbar = 1$. Then note that $\hat{X}$ and $\hat{p}$ satisfy the same commutation relations as $\hat{x}$ and $\hat{p}$ such that the two first terms of (3) describe a quantum harmonic oscillator.

Solution. As in exercise 4.2, the dimer Hamiltonian $\mathcal{H}_0$ may be written in terms of the total spin operator $\vec{S} = \vec{S}_1 + \vec{S}_2$,

$$\mathcal{H}_0 = J\frac{\vec{S}^2}{2} ,$$

where we see that the shift in the energy levels cancels the constant appearing in exercise 4.2.

Let us now set $\hbar = 1$, the correct dependence on $\hbar$ can be restored at any moment by dimensional analysis. Then $\langle\sigma|\vec{S}^2|\sigma\rangle = \hbar^2 S(S+1) = S(S+1)$ with $S = 0, 1$ for the singlet and a triplet state, respectively, so that $\hat{n}_t = \vec{S}^2/2$ is just the projection operator onto the triplet subspace, i.e.

$$\langle\sigma|\hat{n}_t|\sigma\rangle = \begin{cases} 1 & \text{if } \sigma \text{ is a triplet,} \\ 0 & \text{if } \sigma \text{ is a singlet.} \end{cases}$$

Using this operator, the total Hamiltonian has the expected form

$$\mathcal{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 + J\left(1 - \lambda\hat{x}\right)\hat{n}_t = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{X}^2 + \tilde{J}\hat{n}_t,$$

where we have "completed the square", defining

$$\hat{X} = \hat{x} - \frac{J\lambda}{m\omega^2}\hat{n}_t\ , \quad \tilde{J} = J\left(1 - \frac{J\lambda^2}{2m\omega^2}\right), \tag{S.8}$$

and used the fact that $\hat{n}_t$ is indeed a projection, such that $\hat{n}_t^2 = \hat{n}_t$.

It is trivial to see that $\hat{X}$ and $\hat{p}$ satisfy the same commutation relation as $\hat{x}$ and $\hat{p}$. Therefore we may introduce the corresponding raising and lowering operators

$$\hat{a} = \sqrt{\frac{m\omega}{2}}\left(\hat{X} + \frac{i}{m\omega}\hat{p}\right), \qquad \hat{a}^\dagger = \sqrt{\frac{m\omega}{2}}\left(\hat{X} - \frac{i}{m\omega}\hat{p}\right),$$

using which the Hamiltonian can be written as:

$$\mathcal{H} = \underbrace{\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)}_{\mathcal{H}_{\text{harm. osc.}}} + \underbrace{\tilde{J}\hat{n}_t}_{\mathcal{H}_{\text{dimer}}}\ . \tag{S.9}$$

The canonical partition sum is then

$$Z = \mathrm{tr} e^{-\beta\mathcal{H}} = \sum_{n=0}^{\infty}\sum_{\sigma}\langle n, \sigma|e^{-\beta\mathcal{H}}|n, \sigma\rangle\ ,$$

where $|n\rangle$ denotes the eigenstates of $\hat{a}^\dagger\hat{a}$. We observe that the harmonic oscillator term (depending on n) commutes with the spin dimer term (depending on σ) in the Hamiltonian. Therefore, the partition function factorizes as $Z = Z_{\text{harm. osc.}} \cdot Z_{\text{dimer}}$, where we have

$$Z_{\text{harm. osc.}} = \sum_{n=0}^{\infty}\langle n|\mathrm{e}^{-\beta\,\mathcal{H}_{\text{harm. osc.}}}|n\rangle = \sum_{n=0}^{\infty}\mathrm{e}^{-\beta\,\omega\left(n+\frac{1}{2}\right)} = \mathrm{e}^{-\beta\omega/2}\frac{1}{1 - \mathrm{e}^{-\beta\omega}}\ , \tag{S.10}$$

and

$$Z_{\text{dimer}} = \sum_{\sigma}\langle\sigma|\mathrm{e}^{-\beta\mathcal{H}_{\text{dimer}}}|\sigma\rangle = \underbrace{1}_{\substack{\text{singlet state}\\ \hat{n}_t=0}} + \underbrace{3\mathrm{e}^{-\beta\tilde{J}}}_{\substack{\text{triplet states}\\ \hat{n}_t=1}}\ .$$

We finally have

$$Z = Z_{\text{harm. osc.}} \cdot Z_{\text{dimer}} = \frac{e^{-\beta\omega/2}}{1 - e^{-\beta\omega}}\left(1 + 3e^{-\beta\tilde{J}}\right)\ . \tag{S.11}$$

We can then obtain the internal energy as

$$\begin{aligned} U &= -\frac{\partial}{\partial\beta}\log Z = -\frac{\partial}{\partial\beta}\log Z_{\text{harm. osc.}} - \frac{\partial}{\partial\beta}\log Z_{\text{dimer}} \\ &= \frac{\omega}{2} + \frac{\omega}{e^{\beta\omega} - 1} + \frac{3\tilde{J}}{e^{\beta\tilde{J}} + 3} = \frac{\omega}{2}\coth\frac{\beta\omega}{2} + \frac{3\tilde{J}}{e^{\beta\tilde{J}} + 3}. \end{aligned}$$

The specific heat, the free energy and the entropy can be readily computed and are given by

$$\begin{aligned} C &= \frac{\partial U}{\partial T} = C_{\text{harm. osc.}} + C_{\text{dimer}} \\ &= \frac{\omega^2}{4k_BT^2}\frac{1}{\sinh^2(\beta\omega/2)} + \frac{3\tilde{J}^2}{k_BT^2}\frac{e^{\beta\tilde{J}}}{(e^{\beta\tilde{J}} + 3)^2}, \\ F &= -k_BT\log Z = F_{\text{harm. osc.}} + F_{\text{dimer}} \\ &= \frac{\omega}{2} + k_BT\log(1 - e^{-\beta\omega}) - k_BT\log(1 + 3e^{-\beta\tilde{J}}), \\ S &= \frac{U - F}{T} = \frac{\omega}{T(e^{\beta\omega} - 1)} - k_B\log(1 - e^{-\beta\omega}) + \frac{3\tilde{J}}{T(e^{\beta\tilde{J}} + 3)} + k_B\log(1 + 3e^{-\beta\tilde{J}}). \end{aligned}$$

Note that the first two terms of the entropy always vanish in the limit $T \to 0$. As long as $\tilde{J}$ is positive, it is easy to see that the third term also vanishes in the low temperature limit, such that $\lim_{T\to 0} S = 0$. In particular, this is the case for $\lambda = 0$, where $\tilde{J} = J$.

If we make λ large enough, namely $\lambda > \lambda_c := \sqrt{2m\omega^2/J}$, then $\tilde{J}$ becomes negative and the low temperature limit of the entropy entropy becomes

$$\lim_{T\to 0} S = \lim_{T\to 0} \left(\frac{\tilde{J}}{T} + k_B \log 3e^{-\tilde{J}/k_B T} \right) = k_B \log 3.$$

For $\lambda = \lambda_c$, $\tilde{J}$ is equal to zero and $\lim_{T\to 0} S = k_B \log 4$.

This result corresponds, of course, to the number of degenerate ground-states for the spin configuration: For positive $\tilde{J}$, the ground-state is unique (the singlet) and thus the entropy has to vanish as $T \to 0$. For negative $\tilde{J}$, the ground-state is the triplet and thus three-fold degenerate. When there is no effective coupling between the spins then there are four degenerate ground-states, leading to an entropy of $k_B \log 4$.

(b) Calculate the expectation value of the distance between the two spins, $\langle d + \hat{x} \rangle$, as well as $\langle (d + \hat{x})^2 \rangle$. How are these quantities affected by a magnetic field in z-direction, i.e., by adding an additional term in (2) of the form

$$\mathcal{H}_m = -g\mu_B H \sum_i \hat{S}_i^z \quad ?$$

Hints. Write first these expectation values in terms of $\langle \hat{n}_t \rangle$, which you can calculate explicitly. Recall that for a harmonic oscillator, $\langle \hat{X} \rangle$ vanishes, as well as $\langle \hat{a} \rangle$, $\langle \hat{a}^2 \rangle$ etc.

Then recalculate the partition function, adding the magnetic field term and see how this affects $\langle \hat{n}_t \rangle$.

Solution. The mean distance between the two sites is given by

$$\langle d + \hat{x} \rangle = \left\langle d + \hat{X} + \frac{J\lambda}{m\omega^2} \hat{n}_t \right\rangle = d + \frac{J\lambda}{m\omega^2} \langle \hat{n}_t \rangle,$$

where we used (S.8) and the fact that the expectation value of the (shifted) position operator $\hat{X}$ for the harmonic oscillator vanishes. Since the $\hat{n}_t$ only depends on the spin, we can compute its expectation value as

$$\langle \hat{n}_t \rangle = \frac{1}{Z_{\text{dimer}}} \sum_\sigma \langle \sigma | \hat{n}_t e^{-\beta \tilde{J} \hat{n}_t} | \sigma \rangle = \frac{3e^{-\beta \tilde{J}}}{Z_{\text{dimer}}} = \frac{3e^{-\beta \tilde{J}}}{1 + 3e^{-\beta \tilde{J}}}. \tag{S.12}$$

Therefore, we find for the expectation value of the distance between the two spins

$$\langle d + \hat{x} \rangle = d + \frac{J\lambda}{m\omega^2} \frac{3}{e^{\beta \tilde{J}} + 3}.$$

We further compute

$$\langle (d + \hat{x})^2 \rangle = \left\langle \left(d + \hat{X} + \frac{J\lambda}{m\omega^2} \hat{n}_t \right)^2 \right\rangle = d^2 + \langle \hat{X}^2 \rangle + \frac{J\lambda}{m\omega^2} \left(2d + \frac{J\lambda}{m\omega^2} \right) \langle \hat{n}_t \rangle, \tag{S.13}$$

where we have already omitted terms linear in $\hat{X}$ and used that $\hat{n}_t^2 = \hat{n}_t$. For a harmonic oscillator,

$$\langle \hat{X}^2 \rangle = \langle \left(\frac{1}{\sqrt{2m\omega}} \left(\hat{a} + \hat{a}^\dagger \right) \right)^2 \rangle = \frac{1}{m\omega} \langle \hat{a}^\dagger \hat{a} + \frac{1}{2} \rangle = \frac{1}{m\omega} \left(\frac{1}{2} + \frac{1}{e^{\beta\omega} - 1} \right) , \tag{S.14}$$

because $\hat{a}^\dagger\hat{a}$ is the bosonic number operator of the harmonic oscillator, and we know that its average gives the Bose statistics,[2] such that

$$\langle (d+\hat{x})^2\rangle = d^2 + \frac{1}{m\omega}\left(\frac{1}{2}+\frac{1}{e^{\beta\omega}-1}\right) + \frac{J\lambda}{m\omega^2}\left(2d+\frac{J\lambda}{m\omega^2}\right)\langle \hat{n}_t\rangle \ , \tag{S.15}$$

with $\langle \hat{n}_t\rangle$ given by (S.12).

In the presence of a magnetic field, we first recalculate the partition function as

$$\begin{aligned} Z_{\text{dimer with } H} &= \operatorname{tr} \mathrm{e}^{-\beta\left(\tilde{J}\,\hat{n}_t - g\mu_B H\, S^z_{\text{tot}}\right)} = 1 + \mathrm{e}^{-\beta\tilde{J}\,\hat{n}_t}\left(\mathrm{e}^{-\beta g\mu_B H} + 1 + \mathrm{e}^{\beta g\mu_B H}\right) \\ &= 1 + \mathrm{e}^{-\beta\tilde{J}\,\hat{n}_t}\left(1 + 2\cosh\left(\beta g\mu_B H\right)\right) \ , \end{aligned} \tag{S.16}$$

such that $\langle \hat{n}_t\rangle$ becomes

$$\langle \hat{n}_t\rangle = \frac{1}{Z_{\text{dimer with } H}}\sum_\sigma \langle\sigma|\,\hat{n}_t\, e^{-\beta(\tilde{J}\hat{n}_t+\mathcal{H}_m)}|\sigma\rangle = \frac{e^{-\beta\tilde{J}}\left(1+2\cosh(\beta g\mu_B H)\right)}{1+e^{-\beta\tilde{J}}\left(1+2\cosh(\beta g\mu_B H)\right)}. \tag{S.17}$$

Note that $\langle \hat{n}_t\rangle$ is a monotonously increasing function of $|H|$. Thus, by applying a magnetic field we can populate the triplet states and thereby increase the distance between the spins. This effect is called *magnetostriction.*

(c) If the two sites are oppositely charged with charge $\pm q$, the dimer forms a dipole with moment $P = q\,\langle d+\hat{x}\rangle$. This dipole moment can be measured by applying an electric field E along the x-direction, resulting in the additional Hamiltonian term

$$\mathcal{H}_{\text{el}} = -q(d+\hat{x})E \ . \tag{4}$$

Calculate the susceptibility of the dimer at zero electric field,

$$\chi_0^{(\text{el})} = -\left.\frac{\partial^2 F}{\partial E^2}\right|_{E=0} \ , \tag{5}$$

and show that the simple form of the fluctuation-dissipation theorem, which asserts that

$$\chi_0^{(\text{el})} \propto \left\langle (d+\hat{x})^2\right\rangle - \left\langle d+\hat{x}\right\rangle^2 \ , \tag{6}$$

is not valid here.

Hint. Redo the calculations from (a) with $\mathcal{H}_{el}$ included (but without magnetic field), by completing the square with a different definition of $\hat{X}$ and $\tilde{J}$.

Solution. The Hamiltonian is given by

$$\mathcal{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{X}^2 + \tilde{J}\hat{n}_t - \frac{q^2E^2}{2m\omega^2} - dqE \ , \tag{S.18}$$

where now

$$\hat{X} = \hat{x} - \frac{J\lambda}{m\omega^2}\hat{n}_t - \frac{qE}{m\omega^2} \ , \tag{S.19a}$$

$$\tilde{J} = J\left(1 - \frac{J\lambda^2}{2m\omega^2} - \frac{\lambda qE}{m\omega^2}\right) \ . \tag{S.19b}$$

[2] If you're not convinced, or if you forgot how to prove this:

$$\begin{aligned} \frac{1}{m\omega}\langle \hat{a}^\dagger\hat{a}+\frac{1}{2}\rangle &= \frac{1}{m\omega}\cdot Z^{-1}_{\text{harm. osc.}}\cdot \operatorname{tr}\left[\left(\hat{a}^\dagger\hat{a}+\frac{1}{2}\right)\mathrm{e}^{-\beta\omega\left(\hat{a}^\dagger\hat{a}+\frac{1}{2}\right)}\right] \\ &= \frac{1}{m\omega}\cdot Z^{-1}_{\text{harm. osc.}}\cdot\left(-\frac{1}{\beta}\frac{\partial}{\partial\omega}\operatorname{tr}\left[\mathrm{e}^{-\beta\omega\left(\hat{a}^\dagger\hat{a}+\frac{1}{2}\right)}\right]\right) = -\frac{1}{m\omega}\frac{1}{\beta}\frac{\partial}{\partial\omega}\log Z_{\text{harm. osc.}} \\ &= -\frac{1}{m\omega}\frac{1}{\beta}\left(-\frac{\beta}{2} - \frac{1}{1-\mathrm{e}^{-\beta\omega}}\cdot\left(-\mathrm{e}^{-\beta\omega}\right)\cdot(-\beta)\right) = \frac{1}{m\omega}\left(\frac{1}{2}+\frac{1}{e^{\beta\omega}-1}\right) \ . \end{aligned}$$

In the same way as in (a), we find that the partition sum is given by

$$Z = \frac{e^{-\beta\omega/2}}{1-e^{-\beta\omega}} \left(1 + 3e^{-\beta\tilde{J}}\right) e^{\beta\left(dqE + q^2E^2/(2m\omega^2)\right)} \ ,$$

and the free energy is therefore

$$F = -dqE - \frac{q^2E^2}{2m\omega^2} + \frac{\omega}{2} + k_BT\log(1-e^{-\beta\omega}) - k_BT\log(1+3e^{-\beta\tilde{J}}).$$

In order to compute the susceptibility, we have to differentiate the free energy twice with respect to the electric field E. Only for the last term this is somewhat non-trivial: the first differentiation yields

$$\frac{\partial}{\partial E} k_\mathrm{B}T\log(1+3e^{-\beta\tilde{J}}) = \frac{3}{e^{\beta\tilde{J}}+3} J\frac{\lambda q}{m\omega^2} = \frac{J\lambda q}{m\omega^2}\frac{3}{e^{\beta\tilde{J}}+3}.$$

Taking another derivative we find that

$$\frac{\partial^2}{\partial E^2} k_\mathrm{B}T\log(1+3e^{-\beta\tilde{J}}) = \beta\left(\frac{J\lambda q}{m\omega^2}\right)^2 \frac{3e^{\beta\tilde{J}}}{\left(e^{\beta\tilde{J}}+3\right)^2}.$$

For $E=0$, this can simply be expressed in terms of the mean triplet number,

$$\frac{\partial^2}{\partial E^2}\left(k_\mathrm{B}T\log(1+3e^{-\beta\tilde{J}})\right)\Big|_{E=0} = \beta\left(\frac{J\lambda q}{m\omega^2}\right)^2\left(\langle\hat{n}_t\rangle - \langle\hat{n}_t\rangle^2\right) \ ;$$

indeed, from (S.12), we have

$$\langle\hat{n}_t\rangle - \langle\hat{n}_t\rangle^2 = \frac{3\mathrm{e}^{-\beta\tilde{J}}\left(1+3\mathrm{e}^{-\beta\tilde{J}}\right) - \left(3\mathrm{e}^{-\beta\tilde{J}}\right)^2}{\left(1+3\mathrm{e}^{-\beta\tilde{J}}\right)^2} = \frac{3\mathrm{e}^{-\beta\tilde{J}}}{\left(1+3\mathrm{e}^{-\beta\tilde{J}}\right)^2} = \frac{3\mathrm{e}^{\beta\tilde{J}}}{\left(\mathrm{e}^{\beta\tilde{J}}+3\right)^2} \ . \tag{S.20}$$

Therefore, the susceptbility at zero electric field is given by

$$\chi_0^{(\mathrm{el})} = \frac{q^2}{m\omega^2} + \beta\left(\frac{J\lambda q}{m\omega^2}\right)^2\left(\langle\hat{n}_t\rangle - \langle\hat{n}_t\rangle^2\right). \tag{S.21}$$

If we would try to use the simple form of the fluctuation-dissipation theorem to calculate the susceptibility at zero electric field, we would find using our results from (b) that $\chi_0^{(\mathrm{el})}$ should be proportional to

$$\begin{aligned}
&\langle(d+\hat{x})^2\rangle - \langle(d+\hat{x})\rangle^2 \\
&\qquad = d^2 + \langle\hat{X}^2\rangle + \Big(\frac{J\lambda}{m\omega^2}\Big)\Big(2d + \frac{J\lambda}{m\omega^2}\Big)\langle\hat{n}_t\rangle - d^2 - 2d\Big(\frac{J\lambda}{m\omega^2}\Big)\langle\hat{n}_t\rangle - \Big(\frac{J\lambda}{m\omega^2}\Big)^2\langle\hat{n}_t\rangle^2 \\
&\qquad = \langle\hat{X}^2\rangle + \Big(\frac{J\lambda}{m\omega^2}\Big)^2\left(\langle\hat{n}_t\rangle - \langle\hat{n}_t\rangle^2\right).
\end{aligned} \tag{S.22}$$

But using (S.14) we see that it is not the case.

(d) Proceeding as in Section 2.5.3 of the lecture notes, derives the correct fluctuation-dissipation theorem for this system.

Hint. Choosing the variable $\hat{X}$ from (c) as your fundamental degree of freedom introduces a dependence on E in $\hat{x}$, and hence in the coupling (4).

Solution. The simple form of the fluctuation-dissipation theorem is actually only valid for classical systems and simple quantum systems. A first indication that the simple fluctuation-dissipation theorem will not work in our case is the fact that the coupling $(d+\hat{x})$ does not commute with the rest of the Hamiltonian.

In section 2.5.3 of the lecture notes, the fluctuation-dissipation theorem is derived for a magnetization M produced in response to a magnetic field H with some susceptibility χ_M. Here, a distance $(d+\hat{x})$ is produced in response to an electric field E with some susceptibility $\chi_0^{(\mathrm{el})}$. In both situations, we have added a linear coupling term to the Hamiltonian of the form $-M\cdot H$, respectively $-q\,(d+\hat{x})\cdot E$. However, the "correct" degree of freedom of the harmonic oscillator is $\hat{X}$, and not $\hat{x}$. The difference is that with this variable, $\hat{x}$ *depends on* E through equation (S.19a), while M was independent of H.

Proceeding as for the magnetization case, we write

$$0 = \mathrm{tr}\left\{ \left(\langle d + \hat{x} \rangle - (d + \hat{x}) \right) \mathrm{e}^{\beta(F-\mathcal{H})} \right\} \ , \tag{S.23}$$

and will differentiate this equation by E. Notice a first difference with the magnetization case: While we had $M = -\frac{\partial \mathcal{H}}{\partial H}$, if we calculate $\frac{\partial \mathcal{H}}{\partial E}$ we obtain

$$\frac{\partial \mathcal{H}}{\partial E} = -q\left(\frac{qE}{m\omega^2} + d - \frac{J\lambda}{m\omega^2}\,\hat{n}_t \right) = -q\,(d + \hat{x}) + q\hat{X} \ , \tag{S.24}$$

where we used (S.19a). The additional term comes exactly from the dependence of $\hat{x}$ on E. Note that this quantity is proportional to $\hat{n}_t$ and commutes with original Hamiltonian. We also compute [3]

$$\frac{\partial F}{\partial E} = \left\langle \frac{\partial \mathcal{H}}{\partial E} \right\rangle = -q\,\langle d + \hat{x} \rangle \ , \tag{S.25}$$

and

$$\frac{\partial}{\partial E}\,(d + \hat{x}) = \frac{\partial}{\partial E}\left(d + \hat{X} + \frac{Jq}{m\omega^2}\hat{n}_t + \frac{qE}{m\omega^2} \right) = \frac{q}{m\omega^2} \ .$$

Now, differentiating expression (S.23) by E we obtain [4]

$$\begin{aligned} 0 = \frac{\partial}{\partial E}\,\mathrm{tr}\left\{ \left(\langle d + \hat{x} \rangle - (d + \hat{x}) \right) \mathrm{e}^{\beta(F-\mathcal{H})} \right\} &= \mathrm{tr}\left\{ \left(\frac{\partial \langle d + \hat{x} \rangle}{\partial E} - \frac{\partial}{\partial E}\,(d + \hat{x}) \right) \mathrm{e}^{\beta(F-\mathcal{H})} \right\} \\ &+ \mathrm{tr}\left\{ \left[\langle d + \hat{x} \rangle - (d + \hat{x}) \right] \mathrm{e}^{\beta(F-\mathcal{H})} \cdot \beta \cdot \left(-q\langle d + \hat{x} \rangle + q\left(d + \hat{x} - \hat{X} \right) \right) \right\} \ . \end{aligned} \tag{S.28}$$

The second term is obtained using

$$\frac{\partial}{\partial E}\mathrm{e}^{\beta(F-\mathcal{H})} = \frac{\partial}{\partial E}\mathrm{e}^{\beta F}\mathrm{e}^{-\beta\mathcal{H}} = \mathrm{e}^{\beta F}\beta\left(\frac{\partial F}{\partial E} \right)\mathrm{e}^{-\beta\mathcal{H}} + \mathrm{e}^{\beta F}\,(-\beta)\,\mathrm{e}^{-\beta\mathcal{H}}\frac{\partial \mathcal{H}}{\partial E} = \beta\mathrm{e}^{\beta(F-\mathcal{H})}\left(\frac{\partial F}{\partial E} - \frac{\partial \mathcal{H}}{\partial E} \right) \ ,$$

keeping in mind that F is a scalar, not an operator. Continuing from (S.28), we find that

$$\begin{aligned} -\frac{1}{q}\frac{\partial^2 F}{\partial E^2} - \frac{q}{m\omega^2} &= \beta \cdot q \cdot \left\langle \left[\langle d + \hat{x} \rangle - (d + \hat{x}) \right]^2 + \hat{X}\left[\langle d + \hat{x} \rangle - (d + \hat{x}) \right] \right\rangle \\ &= \beta q \left\langle \left[\langle d + \hat{x} \rangle - (d + \hat{x}) \right]^2 \right\rangle + \beta q \left\langle \hat{X}\left[\hat{X} + \frac{J\lambda}{m\omega^2}\hat{n}_t + \frac{qE}{m\omega^2} \right] \right\rangle \\ &= \beta q\left[\left\langle (d + \hat{x})^2 \right\rangle - \langle d + \hat{x} \rangle^2 \right] + \beta q\,\langle \hat{X} \rangle, \end{aligned}$$

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[3] In general, for an external parameter E the Hamiltonian can depend on, one has

$$\frac{\partial F}{\partial E} = -\frac{1}{\beta}\frac{\partial}{\partial E}\log Z = -\frac{1}{\beta}\frac{1}{Z}\frac{\partial}{\partial E}\,\mathrm{tr}\left[\mathrm{e}^{-\beta\mathcal{H}} \right] = \frac{1}{Z}\,\mathrm{tr}\left[\mathrm{e}^{-\beta\mathcal{H}}\frac{\partial \mathcal{H}}{\partial E} \right] = \left\langle \frac{\partial \mathcal{H}}{\partial E} \right\rangle \ ,$$

where the differentiation inside the trace can be justified by using the Taylor expansion of the exponential and using the cyclicity of the trace, without assuming that $[\mathcal{H}, \frac{\partial \mathcal{H}}{\partial E}] = 0$.

[4] The differentiation of the operators inside the second trace of equation (S.28) needs a little bit of justification. First, we can rely on some basic differentiation rules for operators such as

$$\frac{\partial}{\partial E}\,\mathrm{tr}\,(\ldots) = \mathrm{tr}\,\frac{\partial}{\partial E}\,(\ldots) \qquad \text{and} \qquad \frac{\partial}{\partial E}\,(AB) = \frac{\partial A}{\partial E}\,B + A\frac{\partial B}{\partial E} \ .$$

Then, in general, for an operator A and a function f, one has that

$$\frac{\partial}{\partial E}f(A) = \sum_n c_n \frac{\partial}{\partial E}A^n = \sum_n c_n \left(\frac{\partial A}{\partial E}A^{n-1} + A\frac{\partial A}{\partial E}A^{n-2} + \ldots \right) \ , \tag{S.26}$$

where c_n are the coefficients of the Taylor expansion of f. Now, assuming that $[A, \frac{\partial A}{\partial E}] = 0$, we see that $\frac{\partial A}{\partial E}$ commutes through the A's and we can write

$$\frac{\partial}{\partial E}f(A) = \sum_n c_n n A^{n-1}\,\frac{\partial A}{\partial E} = f'(A)\,\frac{\partial A}{\partial E} \ . \tag{S.27}$$

In our case, we have that $\frac{\partial \mathcal{H}}{\partial E} \propto \hat{n}_t$ commutes with $\mathcal{H}$, and so $\frac{\partial}{\partial E}\mathrm{e}^{-\beta\mathcal{H}} = -\beta\mathrm{e}^{-\beta\mathcal{H}} \cdot \frac{\partial \mathcal{H}}{\partial E}$. Note, crucially, that had we chosen to work with the other degree of freedom $\hat{x}$ (having $\hat{X}$ depend on E and not $\hat{x}$), we would have had $\frac{\partial H}{\partial E} = -q\,(d + \hat{x})$, which obviously does not commute with $\mathcal{H}$.

where we have used that $\frac{\partial \langle d+\hat{x}\rangle}{\partial E} = -\frac{1}{q}\frac{\partial}{\partial E}\frac{\partial F}{\partial E} = -\frac{1}{q}\frac{\partial^2 F}{\partial E^2}$, expressed $\hat{x}$ as function of $\hat{X}$ using (S.19a), repeatedly used $\langle \hat{X} \rangle = 0$, and noticed also that $\langle \hat{X}\hat{n}_t \rangle = \langle \hat{X} \rangle_{\text{harm. osc.}} \langle \hat{n}_t \rangle_{\text{dimer}} = 0$, since $\hat{X}$ and $\hat{n}_t$ act on different subsystems. We finally obtain

$$\frac{\chi_0^{(\text{el})}}{\beta q^2} - \frac{1}{\beta m \omega^2} = \left[\left\langle (d+\hat{x})^2 \right\rangle - \langle d+\hat{x} \rangle^2 \right] + \langle \hat{X}^2 \rangle \ , \tag{S.29}$$

which is the *correct* fluctuation-dissipation theorem for this system and agrees with our previous expressions (S.21) and (S.22).