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3.22 The restoring force of an anharmonic oscillator is proportional to the cube of the displacement. Show that the mean kinetic energy of the oscillator is twice its mean potential energy.

$$F \propto q^3 \tag{1}$$
$$F = kq^3 \tag{2}$$
$$U = -\int F dq \tag{3}$$
$$U = -\int kq^3 dq \tag{4}$$
$$U = -\frac{1}{4}kq^4 \tag{5}$$

Knowing this, we can find the Hamiltonian of the system.

$$H = \frac{p^2}{2m} - \frac{1}{4}kq^4 \tag{6}$$

Use the hamiltonian to find the mean kinetic energy.

$$\langle K \rangle = \left\langle \frac{p^2}{2m} \right\rangle \tag{7}$$
$$\langle K \rangle = \left\langle \frac{1}{2}p\frac{p}{m} \right\rangle \tag{8}$$
$$\langle K \rangle = \frac{1}{2}\left\langle p\frac{\partial H}{\partial p} \right\rangle \tag{9}$$

From equation (3.7.2), we know that:

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \delta_{ij}kT \tag{10}$$

Substitute this in equation (9).

$$\langle K \rangle = \frac{1}{2}(kT) \tag{11}$$
$$\langle K \rangle = \frac{1}{2}kT \tag{12}$$

Now find the mean potential energy.

$$\langle U \rangle = \left\langle -\frac{1}{4}kq^4 \right\rangle \tag{13}$$
$$\langle U \rangle = \left\langle -\frac{1}{4}qkq^3 \right\rangle \tag{14}$$
$$\langle U \rangle = \frac{1}{4}\left\langle q\left(-kq^3\right) \right\rangle \tag{15}$$
$$\langle U \rangle = \frac{1}{4}\left\langle q\frac{\partial H}{\partial q} \right\rangle \tag{16}$$
$$\langle U \rangle = \frac{1}{4}(kT) \tag{17}$$
$$\langle U \rangle = \frac{1}{4}kT \tag{18}$$

Now substitute $\langle K \rangle$ in the above relation for $\langle U \rangle$.

$$\langle U \rangle = \frac{1}{4} (2 \langle K \rangle) \tag{19}$$
$$\langle U \rangle = \frac{1}{2} \langle K \rangle \tag{20}$$

$$\boxed{\langle K \rangle = 2 \langle U \rangle}$$

3.31 Study, along the lines of Section 3.8**, the statistical mechanics of a system of** N **"Fermi oscillators," which are characterized by only two eigenvalues, namely** 0 **and** ϵ**.**
Find the partition function.

$$Q_1 = \sum e^{-\beta E_i} \tag{21}$$
$$Q_1 = e^{-\beta(0)} + e^{-\beta\epsilon} \tag{22}$$
$$Q_1 = 1 + e^{-\beta\epsilon} \tag{23}$$
$$Q_N = (Q_1)^N \tag{24}$$

$$\boxed{Q_N = \left(1 + e^{-\beta\epsilon}\right)^N}$$

Using the partition function, find the Helmholtz free energy.

$$A \equiv -kT \ln Q_N \tag{25}$$
$$A = -kT \ln \left[\left(1 + e^{-\beta\epsilon}\right)^N\right] \tag{26}$$

$$\boxed{A = -NkT \ln \left[1 + e^{-\beta\epsilon}\right]}$$

Find the entropy.

$$S \equiv -\left(\frac{\partial A}{\partial T}\right)_{V,N} \tag{27}$$
$$S = -\frac{\partial}{\partial T}\left(-NkT \ln \left[1 + e^{-\epsilon/kT}\right]\right) \tag{28}$$
$$S = -\left(-Nk \ln \left[1 + e^{-\epsilon/kT}\right] - NkT \left(\frac{e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}}\right)\left(\frac{\epsilon}{kT^2}\right)\right) \tag{29}$$
$$S = Nk \ln \left[1 + e^{-\epsilon/kT}\right] + NkT \left(\frac{e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}}\right)\left(\frac{\epsilon}{kT^2}\right) \tag{30}$$
$$S = Nk \left(\ln \left[1 + e^{-\epsilon/kT}\right] + \frac{T\epsilon e^{-\epsilon/kT}}{kT^2\left(1 + e^{-\epsilon/kT}\right)}\right) \tag{31}$$
$$S = Nk \left(\ln \left[1 + e^{-\epsilon/kT}\right] + \frac{\epsilon}{kT}\frac{e^{-\epsilon/kT}}{1 + e^{-\epsilon/kT}}\right) \tag{32}$$
$$S = Nk \left(\ln \left[1 + e^{-\epsilon/kT}\right] + \frac{\epsilon}{kT}\frac{e^{-\epsilon/kT}\left(e^{\epsilon/kT}\right)}{1 + e^{-\epsilon/kT}\left(e^{\epsilon/kT}\right)}\right) \tag{33}$$
$$S = Nk \left(\ln \left[1 + e^{-\epsilon/kT}\right] + \frac{\epsilon}{kT}\frac{1}{e^{\epsilon/kT} + 1}\right) \tag{34}$$

$$\boxed{S = Nk \left(\ln \left[1 + e^{-\beta\epsilon}\right] + \frac{\beta\epsilon}{e^{\epsilon/kT} + 1}\right)}$$

Find U.

$$U \equiv -\left(\frac{\partial \ln Q}{\partial \beta}\right)_E \tag{35}$$
$$U = -\frac{\partial}{\partial \beta}\left(\ln\left[\left(1+e^{-\beta\epsilon}\right)^N\right]\right) \tag{36}$$
$$U = -N\frac{\partial}{\partial \beta}\left(\ln\left[1+e^{-\beta\epsilon}\right]\right) \tag{37}$$
$$U = -N\frac{e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}}(-\epsilon) \tag{38}$$
$$U = N\epsilon\frac{e^{-\beta\epsilon}\left(e^{\beta\epsilon}\right)}{1+e^{-\beta\epsilon}\left(e^{\beta\epsilon}\right)} \tag{39}$$
$$U = N\epsilon\frac{1}{e^{\beta\epsilon}+1} \tag{40}$$

$$\boxed{U = \frac{N\epsilon}{e^{\beta\epsilon}+1}}$$

Find μ.

$$\mu \equiv \left(\frac{\partial A}{\partial N}\right)_{V,T} \tag{41}$$
$$\mu = \frac{\partial}{\partial N}\left(-NkT\ln\left[1+e^{-\beta\epsilon}\right]\right) \tag{42}$$
$$\mu = -kT\ln\left[1+e^{-\beta\epsilon}\right] \tag{43}$$

$$\boxed{\mu = -kT\ln\left[1+e^{-\beta\epsilon}\right]}$$

Find Pressure.

$$P \equiv \left(\frac{\partial A}{\partial V}\right)_{N,T} \tag{44}$$
$$P = \frac{\partial}{\partial V}\left(-NkT\ln\left[1+e^{-\beta\epsilon}\right]\right) \tag{45}$$
$$P = 0 \tag{46}$$

$$\boxed{P = 0}$$

Find c_V.

$$c_V \equiv \left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{47}$$
$$c_V = \frac{\partial}{\partial T}\left(\frac{N\epsilon}{e^{\beta\epsilon}+1}\right) \tag{48}$$
$$c_V = N\epsilon\frac{\partial}{\partial T}\left(e^{\epsilon/kT}+1\right)^{-1} \tag{49}$$
$$c_V = N\epsilon\frac{-1}{\left(e^{\epsilon/kT}+1\right)^2}\left(e^{\epsilon/kT}\right)\left(\frac{-\epsilon}{kT^2}\right) \tag{50}$$
$$c_V = \frac{e^{\epsilon/kT}}{\left(e^{\epsilon/kT}+1\right)^2}\frac{N\epsilon^2}{kT^2} \tag{51}$$
$$c_V = \frac{e^{\beta\epsilon}}{\left(e^{\beta\epsilon}+1\right)^2}\frac{N\epsilon^2\beta}{T} \tag{52}$$

$$\boxed{c_V = \frac{e^{\epsilon/kT}}{\left(e^{\epsilon/kT}+1\right)^2}\frac{N\beta\epsilon^2}{T}}$$

Find c_P, using $P = 0$ as found in equation (46).

$$c_P \equiv \left(\frac{\partial U}{\partial T}\right)_{N,P} + P\left(\frac{\partial V}{\partial T}\right)_{N,P} \tag{53}$$

$$c_P = \frac{\partial}{\partial T}\left(\frac{N\epsilon}{e^{\beta\epsilon}+1}\right) \tag{54}$$

This is equivalent to c_V.

$$c_P = c_V \tag{55}$$

$$c_P = \frac{e^{\epsilon/kT}}{\left(e^{\epsilon/kT}+1\right)^2}\frac{N\beta\epsilon^2}{T} \tag{56}$$

$$\boxed{c_P = \frac{e^{\epsilon/kT}}{\left(e^{\epsilon/kT}+1\right)^2}\frac{N\beta\epsilon^2}{T}}$$

3.42 Consider the system of N magnetic dipoles, studied in Section 3.10, in the microcanonical ensemble. Enumerate the number of microstates, $\Omega(N,E)$, accessible to the system at energy E and evaluate the quantities $S(N,E)$ and $T(N,E)$. Compare your results with equations (3.10.8) and (3.10.9).
Find $\Omega(N,E)$. By definition:

$$\Omega = \frac{N!}{N_{up}!N_{down}!} \tag{57}$$

Also, N_{down} is merely the difference between the total number of magnetic dipoles, N, and the number of dipoles pointing up, N_{up}.

$$\Omega = \frac{N!}{N_{up}!\left(N - N_{up}\right)!} \tag{58}$$

Relate N_{up} to N by using the total energy E and the energy of the anti-aligned state, ϵ.

$$E = \epsilon N_{up} - \epsilon N_{down} \tag{59}$$

$$E = \epsilon N_{up} - \epsilon\left(N - N_{up}\right) \tag{60}$$

$$E = N_{up}\epsilon - N\epsilon + N_{up}\epsilon \tag{61}$$

$$E = 2N_{up}\epsilon - N\epsilon \tag{62}$$

$$\frac{E}{\epsilon} = 2N_{up} - N \tag{63}$$

$$2N_{up} = \frac{E}{\epsilon} + N \tag{64}$$

$$N_{up} = \frac{E}{2\epsilon} + \frac{N}{2} \tag{65}$$

Use equations (65) and (58) to find Ω.

$$\Omega = \frac{N!}{\left(\frac{E}{2\epsilon}+\frac{N}{2}\right)!\left(N - \frac{E}{2\epsilon} - \frac{N}{2}\right)!} \tag{66}$$

$$\Omega = \frac{N!}{\left(\frac{E}{2\epsilon}+\frac{N}{2}\right)!\left(\frac{N}{2} - \frac{E}{2\epsilon}\right)!} \tag{67}$$

$$\boxed{\Omega = \frac{N!}{\left(\frac{E}{2\epsilon}+\frac{N}{2}\right)!\left(\frac{N}{2}-\frac{E}{2\epsilon}\right)!}}$$

Using equation (67), find the entropy S.

$$S \equiv k\ln\Omega \tag{68}$$

$$S = k\ln\left[\frac{N!}{\left(\frac{E}{2\epsilon}+\frac{N}{2}\right)!\left(\frac{N}{2}-\frac{E}{2\epsilon}\right)!}\right] \tag{69}$$

Invoke Stirling's Approximation on equation (69).

$$S = k\left[\ln[N!] - \ln\left[\left(\frac{E}{2\epsilon}+\frac{N}{2}\right)!\right] - \ln\left[\left(\frac{N}{2}-\frac{E}{2\epsilon}\right)!\right]\right] \tag{70}$$

$$S = k\Bigg[N\ln[N] - N - \left(\frac{E}{2\epsilon}+\frac{N}{2}\right)\ln\left[\left(\frac{E}{2\epsilon}+\frac{N}{2}\right)\right] + \left(\frac{E}{2\epsilon}+\frac{N}{2}\right) \tag{71}$$

$$-\left(\frac{N}{2}-\frac{E}{2\epsilon}\right)\ln\left[\left(\frac{N}{2}-\frac{E}{2\epsilon}\right)\right] + \left(\frac{N}{2}-\frac{E}{2\epsilon}\right)\Bigg] \tag{72}$$

$$S = k\left[N\ln[N] - \left(\frac{N}{2}+\frac{E}{2\epsilon}\right)\ln\left[\frac{N}{2}+\frac{E}{2\epsilon}\right] - \left(\frac{N}{2}-\frac{E}{2\epsilon}\right)\ln\left[\frac{N}{2}-\frac{E}{2\epsilon}\right]\right] \tag{73}$$

$$S = Nk\left[\ln[N] - \left(\frac{1}{2}+\frac{E}{2N\epsilon}\right)\ln\left[\frac{N}{2}+\frac{E}{2\epsilon}\right] - \left(\frac{1}{2}-\frac{E}{2N\epsilon}\right)\ln\left[\frac{N}{2}-\frac{E}{2\epsilon}\right]\right] \tag{74}$$

$$S = Nk\left[\ln[N] - \left(\frac{N\epsilon+E}{2N\epsilon}\right)\ln\left[\frac{N\epsilon+E}{2\epsilon}\right] - \left(\frac{N\epsilon-E}{2N\epsilon}\right)\ln\left[\frac{N\epsilon-E}{2\epsilon}\right]\right] \tag{75}$$

$$\boxed{S = Nk\left[\ln[N] - \left(\frac{N\epsilon+E}{2N\epsilon}\right)\ln\left[\frac{N\epsilon+E}{2\epsilon}\right] - \left(\frac{N\epsilon-E}{2N\epsilon}\right)\ln\left[\frac{N\epsilon-E}{2\epsilon}\right]\right]}$$

This expression for entropy is nearly identical to equation (3.10.9), with the only difference being the term $\ln[N]$ inside the brackets missing in the equation in the book. Now, find temperature.

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial E}\right) \tag{76}$$

$$\frac{1}{T} = \frac{\partial}{\partial E}\left(Nk\left[\ln[N] - \left(\frac{N\epsilon+E}{2N\epsilon}\right)\ln\left[\frac{N\epsilon+E}{2\epsilon}\right] - \left(\frac{N\epsilon-E}{2N\epsilon}\right)\ln\left[\frac{N\epsilon-E}{2\epsilon}\right]\right]\right) \tag{77}$$

$$\frac{1}{T} = Nk\frac{\partial}{\partial E}\left(\ln[N] - \left(\frac{N\epsilon+E}{2N\epsilon}\right)\ln\left[\frac{N\epsilon+E}{2\epsilon}\right] - \left(\frac{N\epsilon-E}{2N\epsilon}\right)\ln\left[\frac{N\epsilon-E}{2\epsilon}\right]\right) \tag{78}$$

$$\frac{1}{T} = Nk\frac{\partial}{\partial E}\left(-\left(\frac{N\epsilon+E}{2N\epsilon}\right)\ln\left[\frac{N\epsilon+E}{2\epsilon}\right] - \left(\frac{N\epsilon-E}{2N\epsilon}\right)\ln\left[\frac{N\epsilon-E}{2\epsilon}\right]\right) \tag{79}$$

$$\frac{1}{T} = -Nk\left(\frac{N\epsilon+E}{2\epsilon}\frac{2N\epsilon}{N\epsilon+E}\frac{1}{2\epsilon} + \frac{1}{2N\epsilon}\ln\left[\frac{N\epsilon+E}{2\epsilon}\right] + \frac{N\epsilon-E}{2N\epsilon}\frac{2\epsilon}{N\epsilon-E}\frac{-1}{2\epsilon} - \frac{1}{2N\epsilon}\ln\left[\frac{N\epsilon-E}{2\epsilon}\right]\right) \tag{80}$$

$$\frac{1}{T} = -Nk\left(\frac{N}{2\epsilon} + \frac{1}{2N\epsilon}\ln\left[\frac{N\epsilon+E}{2\epsilon}\right] - \frac{N}{2\epsilon} - \frac{1}{2N\epsilon}\ln\left[\frac{N\epsilon-E}{2\epsilon}\right]\right) \tag{81}$$

$$\frac{1}{T} = -Nk\left(\frac{1}{2N\epsilon}\ln\left[\frac{N\epsilon+E}{2\epsilon}\right] - \frac{1}{2N\epsilon}\ln\left[\frac{N\epsilon-E}{2\epsilon}\right]\right) \tag{82}$$

$$\frac{1}{T} = -Nk\left(\frac{1}{2N\epsilon}\ln\left[\frac{N\epsilon+E}{2\epsilon}\frac{2\epsilon}{N\epsilon-E}\right]\right) \tag{83}$$

$$\frac{1}{T} = \frac{-Nk}{2N\epsilon}\ln\left[\frac{N\epsilon+E}{N\epsilon-E}\right] \tag{84}$$

$$\frac{1}{T} = \frac{k}{2\epsilon}\ln\left[\frac{N\epsilon-E}{N\epsilon+E}\right] \tag{85}$$

$$\boxed{\frac{1}{T} = \frac{k}{2\epsilon} \ln \left[\frac{N\epsilon - E}{N\epsilon + E}\right]}$$

The expression for temperature is identical to equation (3.10.8) in the book.

1. **Using the expression of entropy for a 2-state paramagnet, $S = k \ln \Omega$, and $\frac{1}{T} = \frac{\partial S}{\partial E}$, derive the expression for E as a function of T.**
Use the expression for temperature, derived from $S = k \ln \Omega$ and $\frac{1}{T} = \frac{\partial S}{\partial E}$, found in the previous problem.

$$\frac{1}{T} = \frac{k}{2\epsilon} \ln \left[\frac{N\epsilon - E}{N\epsilon + E}\right] \tag{86}$$

$$\frac{2\epsilon}{kT} = \ln \left[\frac{N\epsilon - E}{N\epsilon + E}\right] \tag{87}$$

$$\frac{N\epsilon - E}{N\epsilon + E} = \exp\left(\frac{2\epsilon}{kT}\right) \tag{88}$$

$$N\epsilon - E = N\epsilon \exp\left(\frac{2\epsilon}{kT}\right) + E \exp\left(\frac{2\epsilon}{kT}\right) \tag{89}$$

$$-E\left(1 + \exp\left(\frac{2\epsilon}{kT}\right)\right) = N\epsilon\left(\exp\left(\frac{2\epsilon}{kT}\right) - 1\right) \tag{90}$$

$$E = -N\epsilon \frac{\exp\left(\frac{2\epsilon}{kT}\right) - 1}{1 + \exp\left(\frac{2\epsilon}{kT}\right)} \tag{91}$$

$$E = -N\epsilon \tanh \frac{\epsilon}{kT} \tag{92}$$

$$E = -N\mu H \tanh \frac{\mu H}{kT} \tag{93}$$

$$\boxed{E = -N\mu H \tanh \frac{\mu H}{kT}}$$

2. **Cold interstellar molecular clouds often contain the molecule cyanogen (CN), whose first rotational excited states have an energy of 4.7×10^{-4} eV above the ground state. Three such excited states share the same energy. It is known that for every 10 CN on the ground state, about 3 are in the three excited state. To account for the data, astronomers suggested that the molecules might be in thermal equilibrium with some "reservoir" with a well-defined temperature. What is that temperature?**
Find the probability of CN to be one of the three excited states.

$$P_{ex} = \frac{e^{-\beta E}}{\sum_i e^{-\beta E_i}} \tag{94}$$

Now, find the probability for CN to be in the ground state.

$$P_{gr} = \frac{1}{\sum_i e^{-\beta E_i}} \tag{95}$$

It is known that for every 10 molecules in the ground state, there are 3 in one of the excited states.

$$\frac{3P_{ex}}{P_{gr}} = \frac{3}{10} \tag{96}$$

Use this information to find the temperature of the "reservoir."

$$\frac{1}{10} = \frac{e^{-\beta E}}{\sum_i e^{-\beta E_i}} \frac{\sum_i e^{-\beta E_i}}{1} \tag{97}$$

$$\frac{1}{10} = \frac{e^{-\beta E}}{1} \tag{98}$$

$$e^{-\beta E} = \frac{1}{10} \tag{99}$$

$$-\beta E = \ln \frac{1}{10} \tag{100}$$

$$\beta E = \ln 10 \tag{101}$$

$$\beta = \frac{1}{E} \ln 10 \tag{102}$$

$$\frac{1}{kT} = \frac{1}{E} \ln 10 \tag{103}$$

$$T = \frac{E}{k \ln 10} \tag{104}$$

$$\boxed{T = 2.367 \text{ K}}$$

3. A lithium nucleus has 4 spin states: $m = -3/2,\ -1/2,\ 1/2,\ 3/2$. In a lab with magnetic field H, $E = -m\mu H$, and $\mu = 1.03 \times 10^{-7}$ eV/T.

(a) If $H = 7$ T, and $T = 3$ K, calculate the probability of a Li nucleus being in each of its 4 states.

$$P_m = \frac{e^{\frac{-m\mu H}{kT}}}{\sum_i e^{-E_i/kT}} \tag{105}$$

$$P_m = \frac{e^{-\frac{m\mu H}{kT}}}{e^{-\frac{3\mu H}{2kT}} + e^{\frac{-\mu H}{2kT}} + e^{\frac{\mu H}{2kT}} + e^{\frac{3\mu H}{2kT}}} \tag{106}$$

$m = -3/2$:

$$\boxed{P_{m=-3/2} = 0.25105}$$

$m = -1/2$:

$$\boxed{P_{m=-1/2} = 0.25035}$$

$m = 1/2$:

$$\boxed{P_{m=1/2} = 0.24965}$$

$m = 3/2$:

$$\boxed{P_{m=3/2} = 0.24896}$$

(b) If the direction of H is suddenly reversed, what is the temperature of the system?

If H suddenly inverts, these probabilities stay the same.

$$P_{m=-3/2} = 0.25105 \tag{107}$$

$$\frac{e^{-\mu m H/kT}}{4.00002} = 0.25105 \tag{108}$$

$$e^{-\mu(-3/2)H/kT} = 1.00419 \tag{109}$$

$$\frac{3}{2}\mu H \frac{1}{kT} = \ln 1.00419 \tag{110}$$

$$T = \frac{3}{2}\mu\,(-7)\,\frac{1}{k \ln 1.00419} \tag{111}$$

$$\boxed{T = -3\text{ K}}$$

The temperature flips signs!

(c) If it is on a white dwarf where $H = 100$ T, what is the energy difference between the 2 states of its electronic spin? Note, Li has only one electron in its outer shell and it has no orbital angular momentum. So it is spin-only with $s = 1/2$. The magnetic moment μ from an electron is about 1800 times greater than its nuclear moment.

$$E_s = -s\mu_e H \tag{112}$$
$$\mu_e = 1800\mu \tag{113}$$

$s = 1/2$:

$$E_{s=1/2} = -(1/2)\,1800\mu H \tag{114}$$
$$E_{s=1/2} = -(1/2)\,1800\left(1.03 \times 10^{-7}\text{ eV T}^{-1}\right)(100\text{ T}) \tag{115}$$

$$\boxed{E_{s=1/2} = -0.00927\text{ eV}}$$

$s = -1/2$:

$$E_{s=-1/2} = -(-1/2)\,1800\mu H \tag{116}$$
$$E_{s=-1/2} = -(-1/2)\,1800\left(1.03 \times 10^{-7}\text{ eV T}^{-1}\right)(100\text{ T}) \tag{117}$$

$$\boxed{E_{s=-1/2} = 0.00927\text{ eV}}$$

Find the energy difference between the two states.

$$\Delta E = E_{s=-1/2} - E_{s=1/2} \tag{118}$$
$$\Delta E = (0.00927\text{ eV}) - (-0.00927\text{ eV}) \tag{119}$$

$$\boxed{\Delta E = 0.01854\text{ eV}}$$