Statistical Mechanics: **Problem Set 3**

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Sethna problems 3.6, 3.8, 5.1 and 5.5. All final answers are $\boxed{\text{boxed}}$.

1 Connecting two macroscopic systems

An isolated system with energy E is composed of two macroscopic subsystems, each of fixed volume V and number of particles N. The subsystems are weakly couples, so the sum of their energies is $E_1 + E_2 = E$. The volume of the energy surface of a system with the Hamiltonian $\mathcal{H}$ is given by

$$\Omega(E) = \int \frac{\mathrm{d}\mathbb{P}\,\mathrm{d}\mathbb{Q}}{h^{3N}}\ \delta(E - \mathcal{H}(\mathbb{P},\mathbb{Q})) \tag{1.1}$$

$$= \int \frac{\mathrm{d}\mathbb{P}_1\,\mathrm{d}\mathbb{Q}_1}{h^{3N_1}} \frac{\mathrm{d}\mathbb{P}_2\,\mathrm{d}\mathbb{Q}_2}{h^{3N_2}}\ \delta(E - (\mathcal{H}_1(\mathbb{P}_1,\mathbb{Q}_1) + \mathcal{H}_2(\mathbb{P}_2,\mathbb{Q}_2)). \tag{1.2}$$

Derive the formula $\Omega(E) = \int \mathrm{d}E_1\ \Omega_1(E_1)\Omega_2(E-E_1)$, for the volume of the energy surface of the energy surface of the whole system using Dirac δ-functions.

Solution: Beginning with the definition for the volume of the energy surface of a system with Hamiltonian $\mathcal{H}$ [**??**], we insert the identity $\int \mathrm{d}E_1\ \delta(E_1 - \mathcal{H}_1) = 1$. Grouping the integrals together, we notice the definition for $\Omega(E_1)$ where the delta-function picks out $E_1 = \mathcal{H}_1$. We then do the same for the next integral, where the delta-function now picks out $E - E_1 = \mathcal{H}_2$.

$$\Omega(E) = \iiint \mathrm{d}E_1\ \delta(E_1 - \mathcal{H}_1)\ \frac{\mathrm{d}\mathbb{P}_1\,\mathrm{d}\mathbb{Q}_1}{h^{3N_1}} \frac{\mathrm{d}\mathbb{P}_2\,\mathrm{d}\mathbb{Q}_2}{h^{3N_2}}\ \delta(E - (\mathcal{H}_1 + \mathcal{H}_2)) \tag{1.3}$$

$$= \int \mathrm{d}E_1 \int \frac{\mathrm{d}\mathbb{P}_2\,\mathrm{d}\mathbb{Q}_2}{h^{3N_2}}\ \delta(E - (\mathcal{H}_1 + \mathcal{H}_2) \int \frac{\mathrm{d}\mathbb{P}_1\,\mathrm{d}\mathbb{Q}_1}{h^{3N_1}}\ \delta(E_1 - \mathcal{H}_1) \tag{1.4}$$

$$= \int \mathrm{d}E_1\ \Omega(E_1) \int \frac{\mathrm{d}\mathbb{P}_2\,\mathrm{d}\mathbb{Q}_2}{h^{3N_2}} \delta(E - E_1 - \mathcal{H}_2) \tag{1.5}$$

$$\boxed{\Omega(E) = \int \mathrm{d}E_1\ \Omega(E_1)\ \Omega(E - E_1)} \tag{1.6}$$

2 Microcanonical energy fluctuations

For two subsystems with energy E_1 and $E_2 = E - E_1$ the probability density of E_1 is a Gaussian with variance

$$\sigma_{E_1}^2 = -k_B/(\frac{\partial^2 S_1}{\partial E_1^2} + \frac{\partial^2 S_2}{\partial E_2^2}). \tag{2.1}$$

(a) *Show that*

$$\frac{1}{k_B}\frac{\partial^2 S}{\partial E^2} = -\frac{1}{k_B T}\frac{1}{N c_v T} \tag{2.2}$$

where c_v is the inverse of the total specific heat at constant volume.

Solution: The equilibrium entropy is $S = k_B \log(\Omega(E))$ where temperature is defined as $1/T \equiv \partial S/\partial E$. Using some sleight of hand Leibniz notation[1]:

$$\frac{1}{k_B}\frac{\partial^2 S}{\partial E^2} = \frac{1}{k_B}\frac{\partial}{\partial E}\frac{\partial S}{\partial E} \tag{2.3}$$

$$= \frac{1}{k_B}\frac{\partial}{\partial E}\frac{1}{\Omega}\frac{\partial \Omega}{\partial E} \tag{2.4}$$

$$= \frac{1}{k_B}\frac{\partial}{\partial E}\frac{1}{T} = \frac{1}{k_B}\frac{\partial}{\partial E}\frac{\partial T}{\partial T}\frac{1}{T} \tag{2.5}$$

$$= \frac{1}{k_B}\frac{\partial T}{\partial E}\frac{\partial \frac{1}{T}}{\partial T} = -\frac{1}{k_B}\frac{1}{N c_v}\frac{1}{T^2} \tag{2.6}$$

$$\boxed{\frac{1}{k_B}\frac{\partial^2 S}{\partial E^2} = -\frac{1}{k_B T}\frac{1}{N c_v T}} \tag{2.7}$$

where we made use of the specific heat $N c_v \equiv \partial E/\partial T$.

(b) *If c_{v1} and c_{v2} are the specific heats per particle for two subsystems of N particles each, show using eqns [**??**] and [**??**] that*

$$\frac{1}{c_{v1}} + \frac{1}{c_{v2}} = \frac{N k_B T^2}{\sigma_{E_1}^2}. \tag{2.8}$$

Solution: This one is pure massaging equations, specifically [**??**] and [**??**].

$$\sigma_{E_1}^2 = -k_B/\left(\frac{\partial^2 S_1}{\partial E_1^2} + \frac{\partial^2 S_2}{\partial E_2^2}\right) \tag{2.9}$$

$$\frac{\partial^2 S_1}{\partial E_1^2} + \frac{\partial^2 S_2}{\partial E_2^2} = -k_B/\sigma_{E_1}^2 \tag{2.10}$$

We substitute in the specific heat $N c_v$ for each subsystem.

$$-\frac{1}{NT^2}\left(\frac{1}{c_{v1}} + \frac{1}{c_{v2}}\right) = -\frac{k_B}{\sigma_{E_1}^2} \tag{2.11}$$

$$\boxed{\frac{1}{c_{v1}} + \frac{1}{c_{v2}} = \frac{N k_B T^2}{\sigma_{E_1}^2}} \tag{2.12}$$

(c) *Using the equipartition theorem, write the temperature in terms of K. Show that $c_v^{(1)} = 3k_B/2$ for the momentum degrees of freedom. In terms of K and σ_K, solve for the total specific heat of the molecular dynamics simulation.*

Solution:

Temperature in terms of K. The kinetic energy of a particle moving in a direction i is given by $p_i^2/2m$. The average kinetic energy of a particle depends on the temperature of its system $K = 1/2 k_B T$. A particle has three translational degrees of freedom, each of which contribute equally—on average—to the average to the particle's kinetic energy (equipartition theorem). Thus for a gas of N atoms, its total average kinetic energy is

$$K = \frac{3}{2} N k_B T. \tag{2.13}$$

[1] Mathematicians beware!

This allows us to write the temperature as a function of energy as $\boxed{T(K) = \frac{2}{3}\frac{E}{Nk_B}}$.

Momentum degrees of freedom. Remebering the definition of specific heat, we rewrite energy in terms of temperature to show $c_v^{(1)} = 3k_B/2$ for the momentum degrees of freedom.

$$Nc_{v1} = \frac{\partial E}{\partial T_1} = \frac{\partial}{\partial T_1}\left(\frac{3}{2}Nk_b T_1\right) \tag{2.14}$$

$$\boxed{c_{v1} = 3/2k_B} \tag{2.15}$$

Total specific heat. First note that $\sigma_K = \sigma_E$. Let $K = \langle E_1 \rangle$. Since the kinetic energy does not depend on the spacial configuration $\mathbb{Q}$ and potential energy does not depend on momentum configuration $\mathbb{P}$, we can treat our system as two uncoupled-subsystems, where c_{v1} is the kinetic contribution to specific heat and c_{v2} is the configuration contribution. Plug in [**??**] and [**??**] to [**??**].

$$\frac{1}{c_{v2}} = \frac{Nk_B T^2}{\sigma_{E_1}^2} - \frac{2}{3}k_B T \tag{2.16}$$

$$\frac{1}{c_{v2}} = \frac{1}{Nk_B\sigma_{E_1}^2}\left(4K^2 - 6Nk_B^2\sigma_{E_1}^2\right) \tag{2.17}$$

$$c_{v2} = \frac{Nk_B\sigma_{E_1}^2}{4K^2 - 6Nk_B^2\sigma_{E_1}^2} c_{v2} = \frac{(k_B N\sigma_K^2)}{4K^2 - 6N\sigma_K^2} \tag{2.18}$$

Then we find that $c_{v1} + c_{v2}$ is

$$c_v = c_{v1} + c_{v2} \tag{2.19}$$

$$= \frac{(k_B N\sigma_K^2)}{4K^2 - 6N\sigma_K^2} + \frac{3}{2}k_B \tag{2.20}$$

$$\boxed{c_v = k_B \frac{K^2}{\frac{2}{3}K^2 - N\sigma_K^2}} \tag{2.21}$$

3 Life and the heat death of the universe

Living beings intercept entropy flows; they use low-entropy sources of energy and emit high-entropy forms of the same energy. Freeman Dyson presumed that an intelligent being generates a fixed entropy ΔS per thought. Let's investigate how living beings might evolve to cope with the cooling and dimming we expect during the heat death of the Universe.
Assume that a being draws heat Q from a hot reservoir at T_1 and radiates it away to a cold reservoir at T_2.

(a) Energy needed per thought. *What is the minimum energy Q needed per thought, in terms of ΔS and T_2?*

Solution: The change in entropy ΔS is given by

$$\Delta S = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}. \tag{3.1}$$

If our heat bath T_1 is very hot, we can ignore the last tern in [**??**] and we're left with

$$\Delta S = \frac{Q_2}{T_2} \tag{3.2}$$

Thus, the minimum energy Q needed per thought is given by

$$\boxed{Q = T_2 \Delta S.} \tag{3.3}$$

(b) Time needed per thought to radiate energy. *Write an expression for the maximum rate of thoughts per unit time* $\mathrm{d}H/\mathrm{d}t$ *(the inverse of the time Δt per thought), in terms of ΔS, C, and T_2.*

Solution: Let H be number of thoughts. Dyson shows that power radiated by our intelligent-being-as-entropy-producer is about $P = CT_2^3$. It follows that the energy radiated for a thought of time τ is $E = CT_2^3\tau$.

This energy is simply energy Q, the heat energy taken from the hot bath T_1. The time-per-thought τ is

$$\tau = \frac{\Delta S}{CT_2^2} \tag{3.4}$$

The time needed per thought $\mathrm{d}H/\mathrm{d}t$ is [**??**]'s reciprocal.

$$\boxed{\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{CT_2^2}{\Delta S}} \tag{3.5}$$

(c) Number of thoughts for an ecologically efficient being. Our Universe is expanding ($R \sim t$); the microwave background radiation has a characteristic temperature $\Theta(t) \sim R^{-1}$ which is getting lower as the Universe expands due to the Doppler effect. *How many thoughts H can an ecologically efficient being have between now and time infinity, in terms of ΔS, C, A, and the current time t_0?*

Solution: An ecologically efficient being wants to radiate as little heat as possible; we choose T_2 to be equal to the microwave background $\Theta(t)$ since it cannot radiate heat at a temperature below this.

We integrate the rate of thoughts with respect to time to get the number of thoughts H for a given time scale, using $\Theta(t) \sim A/t$.

$$H = \int_{t_0}^{\infty} \mathrm{d}H = \int_{t_0}^{\infty} \mathrm{d}t\, \frac{\mathrm{d}H}{\mathrm{d}t} = \int_{t_0}^{\infty} \mathrm{d}t\, \frac{CT_2^2}{\Delta S} \tag{3.6}$$

$$= \frac{CA^2}{\Delta S}\int_{t_0}^{\infty} \mathrm{d}t\, \frac{1}{t^2} = \frac{CA^2}{\Delta S} t^{-1}\Big|_{\infty}^{t_0} \tag{3.7}$$

The number of thoughts an efficient being can have between now and time infinity is

$$\boxed{H = \frac{CA^2}{\Delta S}\frac{1}{t_0}}. \tag{3.8}$$

(d) Time without end: greedy beings. Dyson would like his beings to be able to think an infinite number of thoughts before the Universe ends, but consume a finite amount of energy. He proposes that beings radiate at a temperature $T_2(t) \sim t^{-3/8}$. *Show that with Dyson's cooling schedule, the total number of H is infinite, but the total energy consumed U is finite.*

Solution: Take $T_2(t) = At^{-3/8}$ and integrate [**??**] to show that the number of thoughts at Dyson's proposed radiation temperature is infinite.

$$H = \int_{t_0}^{\infty} \mathrm{d}t \, \frac{\mathrm{d}H}{\mathrm{d}t} = \frac{CA^2}{\Delta S} \int_{t_0}^{\infty} \mathrm{d}t \left(\frac{1}{t^{3/8}} \right)^2 = \frac{8}{2} \frac{CA^2}{\Delta S} \, t^{1/4} \Big|_{t=t_0}^{t=\infty} = \boxed{\infty} \tag{3.9}$$

However, the total energy consumed is still finite. The total energy consumed U is equal to the number of thoughts [**??**] multiplied the energy per thought [**??**].

$$\frac{\mathrm{d}U}{\mathrm{d}t} = Q\frac{\mathrm{d}H}{\mathrm{d}t} = T_2 \Delta S \frac{\mathrm{d}H}{\mathrm{d}t} = CT_2^3 \tag{3.10}$$

$$U = CA^3 \int_{t_0}^{\infty} \mathrm{d}t \left(\frac{1}{t^{3/8}} \right)^3 = CA^3 \int_{t_0}^{\infty} \mathrm{d}t \; t^{-9/8} = 8CA^3 t^{-1/8} \Big|_{\infty}^{t_0} \tag{3.11}$$

We find that the total energy consumed is finite.

$$\boxed{U = 8CA^3 \; t_0^{-1/8}} \tag{3.12}$$

4 Pressure-volume diagrams

A monatomic ideal gas in a piston is cycled around the path in the $P-V$ diagram in fig. ??. Leg **a** cools at constant volume by connecting to a heat bath at T_c; leg **b** heats at a constant pressure by connecting to a heat bath at T_h; leg **c** compresses at constant temperature while remaining connected to the bath at T_h.

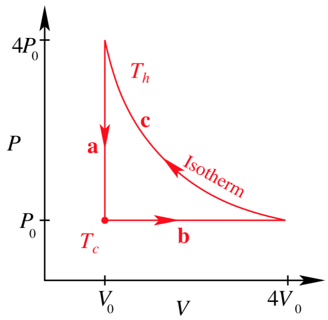

Figure 1: $P-V$ diagram.

Which of the following six statements are true?

(1) The cycle is reversible; no net entropy is created in the Universe.
False. Leg **a** and leg **b** both increase net entropy of the universe. The system is exchanging heat with a cold and hot bath, respectively, leading to an entropy increase of $\Delta S = \Delta Q/T$.

(2) The cycle acts as a refrigerator, using work from the piston to draw energy from the cold bath into the bot bath, cooling the bath.
False. In leg **a**, when the system is in contact with the cold bath, heat energy is being transferred *from* the system *to* the cold bath.

(3) The cycle acts as an engine, transfering heat from the hot bath to the cold bath and doing positive net work on the outside world.
False. $W = \int P\,\mathrm{d}V < 0$; the work done on the outside world is negative. Engines do positive work on their environments.

(4) The work done per cycle has magnitude $|W| = P_0V_0|4\log 4 - 3|$.
True. It can be shown that the area integral $\int P\,\mathrm{d}V$ is equal to $P_0V_0|4\log 4 - 3|$ (i did it on the white board in discussion!).

(5) The heat transferred into the cold bath, Q_c, has magnitude $|Q_c| = (9/2)P_0V_0$.
True. Consider leg **a** (where no work is being done). The heat energy transferred is given by $Q = \Delta U - W$. Initially, the potential energy is $U_i = (3/2)NK_bT_h = (3/2)4P_0V_0$. Once the cycle reaching leg **b**, the potential energy is $U_f = (3/2)NK_bT_c = (3/2)P_0V_0$. Therefore, $Q = \Delta U = (9/2)P_0V_0$.

(6) The heat transferred from the hot bath, Q_h, plus the net work W done by the piston onto the gas, equals the heat Q_c transferred into the cold bath.
True. This is a statement of total energy conservation in the system.