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Course: **8.333 - Statistical Mechanics I**
Problem set: **#1**

1. Non-Carnot Engine. According to Clausius's theorem, we have

$$\oint \frac{dQ}{T} \le 0 \implies \sum_\alpha \frac{Q_\alpha^+}{T_\alpha^+} - \sum_\beta \frac{Q_\beta^-}{T_\beta^-} \le 0.$$

From here, we find that

$$\frac{Q^+}{T_{\max}} = \frac{1}{T_{\max}} \sum_\alpha Q_\alpha^+ \le \sum_\alpha \frac{Q_\alpha^+}{T_\alpha^+} \le \sum_\beta \frac{Q_\beta^-}{T_\beta^-} \le \frac{1}{T_{\min}} \sum_\beta Q_\beta^- = \frac{Q^-}{T_{\min}}.$$

Thus, we have

$$\eta = \frac{Q^+ - Q^-}{Q^+} = 1 - \frac{Q^-}{Q^+} \le 1 - \frac{T_{\min}}{T_{\max}} = \eta_{\text{Carnot}},$$

as desired.

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2. Heat exchange between identical bodies.

(a) Assuming perfect heat exchange, any two identical bodies at temperatures θ_1, θ_2 coming into contact will reach a final temperature of $(\theta_1 + \theta_2)/2$. In general, for n bodies at temperatures $\{\theta_1, \ldots, \theta_n\}$, the final temperature solves the following equation which equates the initial and final heat energies:

$$C \sum_{i=1}^n \theta_i = CnT_F \implies \boxed{T_F = \frac{1}{n} \sum_{i=1}^n \theta_i}$$

Thus, T_F is the mean of the initial temperatures. The total change in entropy can be computed as follows:

$$\Delta S = \sum_{i=1}^n \Delta S_i = \sum_{i=1}^n \int_{\theta_i}^{T_F} \frac{C dT}{T} = C \sum_i \ln\left(\frac{T_F}{T_i}\right) = \boxed{C \ln\left(\frac{T_F^n}{\prod_{i=1}^n \theta_i}\right)}$$

(b) If all heat transfer is done via Carnot engines, then $\Delta S = 0$ since Carnot engines are reversible. This implies that the final temperature T_F is the geometric mean of the initial temperatures.

$$\boxed{T_F = \left(\prod_{i=1}^n \theta_i\right)^{1/n}}$$

The amount of work done by the engine is simply the difference in energy:

$$\boxed{W = C \sum_{i=1}^n \theta_i - Cn \left(\prod_{i=1}^n \theta_i\right)^{1/n}}$$

Alternatively, one could obtain this result by calculating the amount of heat Q^+ flowing into the engines and Q^- leaving the engines. Their difference $Q^+ - Q^-$ is the work done by the engines.

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(c) Suppose without loss of generality that body 1 is at the theoretical maximum T_H. It follows that the remaining $(n-1)$ bodies must be at some equilibrium temperature T_E, since otherwise one can run a Carnot engine between two bodies of different temperatures and extract positive work to increase T_H further, a contradiction. To bring $\theta_2, \ldots, \theta_n$ to this minimum equilibrium temperature T_E, we first must use a Carnot engine (since they are most efficient) to bring $(n-1)$ bodies to some intermediate temperature T_I. Next, we use the work generated by this process to pump heat away from the $(n-1)$ bodies at T_I into body 1 using another Carnot engine, putting the $(n-1)$ bodies at their final temperature T_F and body 1 at the theoretical maximum T_H. The net result of this process is conservation of energy (since no work gets recycled and reused) and conservation of entropy (since all heat transfers are by Carnot engines/refrigerators). As a result, we have two equations:

$$\boxed{T_F = \frac{1}{n-1}\left(\sum_{i=1}^{n} \theta_i - T_H\right)} \quad \text{and} \quad \ln\frac{T_H}{\theta_1} + \ln\frac{T_F^{n-1}}{\prod_{i=2}^{n}\theta_i} = 0 \implies \ln\frac{T_H T_F^{n-1}}{\prod_{i=1}^{n}\theta_i} = 0 \implies \boxed{T_H T_F^{n-1} = \prod_{i=1}^{n}\theta_i}$$

These two together give us an equation for T_H:

$$\boxed{\frac{T_H}{(n-1)^{n-1}}\left(\sum_{i=1}^{n}\theta_i - T_H\right)^{n-1} = \prod_{i=1}^{n}\theta_i}$$

We notice that T_H does **NOT** depend on which body we select as the one to be heated.

(d) With $\theta_1 = \theta_2 = \theta_H$ and $\theta_3 = \theta_C < \theta_H$, we have the following equation:

$$\frac{T_H}{(3-1)^{3-1}}\left[(2\theta_H + \theta_C) - T_H\right]^{3-1} = \theta_H^2 \theta_C.$$

With the help of Mathematica, we find the theoretical maximum T_H to be

$$\boxed{T_H(\theta_H, \theta_C) = \frac{1}{2}\left(\theta_C + 4\theta_H + \sqrt{\theta_C(8\theta_H + \theta_C)}\right)}$$

Mathematica code:

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In[6]:= Solve[
Th*((2*\[Theta]h + \[Theta]c - Th)/(3 -
1))^2 == \[Theta]h^2*\[Theta]c, Th] // FullSimplify

Out[6]= {{Th -> \[Theta]c}, {Th ->
1/2 (\[Theta]c + 4 \[Theta]h -
Sqrt[\[Theta]c] Sqrt[\[Theta]c + 8 \[Theta]h])}, {Th ->
1/2 (\[Theta]c + 4 \[Theta]h +
Sqrt[\[Theta]c] Sqrt[\[Theta]c + 8 \[Theta]h])}}
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3. **Hard core gas.** The equation of state is

$$P(V - Nb) = Nk_B T.$$

(a) Starting with the fundamental relation

$$dE = TdS + \sum_i J_i dx_i + \mu N = TdS - PdV + \mu N$$

we Legendre transform $E \to E - TS$ so that S is no longer an independent variable.

$$d(E - TS) = dF = -SdT - PdV + \mu dN.$$

Since the particle number is fixed, $dN = 0$ and we will drop this term for the rest of the problem. The Maxwell's relation now comes out of the second mixed derivative of F:

$$\left.\frac{\partial^2 F}{\partial V \partial T}\right|_N = \left.\frac{\partial^2 F}{\partial T \partial V}\right|_N \implies \boxed{\left.\frac{\partial S}{\partial V}\right|_{T,N}} = \left.\frac{\partial P}{\partial T}\right|_{V,N} = \left.\frac{\partial}{\partial T}\right|_{V,N}\frac{Nk_B T}{V - Nb} = \frac{Nk_B}{V - Nb} = \boxed{\frac{P}{T}}$$

(b) To calculate $dE(T, N)$, we must replace the independent variable S by T, V, the desired independent variables. To do this, we compute the total differential dS as follows:

$$dS = \frac{\partial S}{\partial V}\bigg|_{T,N} dV + \frac{\partial S}{\partial T}\bigg|_{V,N} dT = \frac{P}{T} dV + \frac{\partial S}{\partial T}\bigg|_{V,N} dT.$$

Plugging this back into the fundamental relation for dE, we find

$$\boxed{dE(T, V) = T\frac{\partial S}{\partial T}\bigg|_{V,N} dT \ (+ \ \mu dN)}$$

So E is a function of T and N only.

(c) We compute the heat capacities as follows, once again setting $dN = 0$:

$$C_P = \frac{dQ}{dT}\bigg|_{P,N} = \frac{dE + PdV}{dT}\bigg|_{P,N} = \frac{dE}{dT}\bigg|_{P,N} + P\frac{dV}{dT}\bigg|_{P,N}$$

$$C_V = \frac{dQ}{dT}\bigg|_{P,N} = \frac{dE + 0}{dT}\bigg|_{V,N} = \frac{dE}{dT}\bigg|_{V,N}.$$

From Part (b), we see that since E only depends on T and N,

$$\frac{dE}{dT}\bigg|_{P,N} = \frac{dE}{dT}\bigg|_{V,N} = C_V,$$

and so

$$C_P = C_V + P\frac{Nk_B}{P} = C_V + Nk_B \implies \boxed{\gamma \equiv \frac{C_P}{C_V} = 1 + \frac{Nk_B}{C_V}}$$

as desired.

(d) From part (c), we know that $\gamma = 1 + Nk_B/C_V$. Now, we need to find $E(P, V)$ or, equivalently, write dE in terms of dV and dP. To do this, we will use the equation of state to express the total differential dT in dP and dV.

$$dE = C_V dT \implies C_V d\left[\frac{P(V - Nb)}{Nk_B}\right] = \frac{C_V}{Nk_B}\left[(V - Nb)dP + PdV\right].$$

Now, the adiabatic condition says

$$dQ = 0 \implies dE + PdV = 0 \implies 0 = \frac{C_V(V - Nb)}{Nk_B}dP + \left(1 + \frac{C_V}{Nk_B}\right)PdV.$$

Rearranging to move P and V to the opposite sides and integrating, we find

$$\int \frac{dP}{P} = \left(1 + \frac{C_V}{Nk_B}\right)\left(\frac{-Nk_B}{C_V}\right)\int \frac{dV}{V - Nb} \implies \ln P = -\gamma \ln(V - Nb) + C$$

and therefore,

$$P(V - Nb)^\gamma = \text{constant},$$

as desired.

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4. Superconducting transition.

(a) By the third law of thermodynamics $S_s(T = 0) = S_n(T = 0) = 0$.

$$\boxed{S_s(T)} = S_s(T) - S_s(0) = \int_0^T \frac{C_s(t)\,dt}{t} = \int_0^T V\alpha t^2\,dt = \boxed{\frac{V\alpha T^3}{3}}$$

$$\boxed{S_n(t)} = S_n(T) - S_n(0) = \int_0^T \frac{C_n(t)\,dt}{t} = \int_0^T V[\beta t^2 + \gamma]\,dt = \boxed{\frac{V\beta T^3}{3} + V\gamma T}$$

(b) Since the latent heat is zero at T_c, we have

$$0 = L = \frac{Q}{m} = \frac{T\Delta S}{m} \implies S_s(T_c) = S_n(T_c) \implies V\alpha T^3 = V\beta T^3 + 3V\gamma T \implies \boxed{T = \sqrt{\frac{3\gamma}{\alpha - \beta}}}$$

(c) Since $dV = 0$, we simply have $dE = T\,dS$. Integrating this equation gives us the internal energy at each phase.

$$\boxed{E_s(T)} = E_s(T = 0) + \int_{S_s(0)}^{S_s(T)} t\,dS_s(t) = E_0 - V\Delta + \int_0^T V\alpha t^3\,dt = \boxed{E_0 - V\Delta + \frac{V\alpha T^4}{4}}$$

$$\boxed{E_n(T)} = E_n(T = 0) + \int_{S_n(0)}^{S_n(T)} t\,dS_n(t) = E_0 + \int_0^T V\beta t^3 + V\gamma t\,dt = \boxed{E_0 + \frac{V\beta T^4}{4} + \frac{V\gamma T^2}{2}}$$

(d) To solve for Δ, we look at the temperature at which phase transition occurs, T_c. During phase transition, $\Delta G(T_c) = 0$. Thus, we have

$$E_s(T) - T_c S_s(T_c) = E_n(T) - T_c S_n(T_c)$$

$$\implies E_0 - V\Delta + \frac{V\alpha T^4}{4} - T_c \frac{V\alpha T^3}{3} = E_0 + \frac{V\beta T^4}{4} + \frac{V\gamma T^2}{2} - T_c\left[\frac{V\beta T^3}{3} + V\gamma T\right]$$

$$\implies \Delta = \frac{\gamma T_c^2}{2V} - \frac{(\alpha - \beta)T_c^4}{12V}.$$

With $T_c = \sqrt{3\gamma/(\alpha - \beta)}$, we find

$$\boxed{\Delta = \frac{3\gamma^2}{4(\alpha - \beta)}}$$

(e) To find the critical magnetic field, we want to equate the Gibbs free energy (as we did before), but this time at temperature T, including the effect of magnetic fields. The Legendre transformation says

$$dG_s = d(E_s - TS - B_s M_s) = -S_s dT - M_s dB_s = -S_s dT + \frac{VB}{4\pi} dB_s.$$

Since $S_s(T)$ is known, we can integrate this equation to find

$$G_s(T) = -\frac{V\alpha T^4}{12} + \frac{VB^2}{8\pi} + E_s(T = 0) = E_0 - V\Delta - \frac{V\alpha T^4}{12} + \frac{VB^2}{8\pi}.$$

Similarly, the Gibbs free energy for the normal phase can be calculated. This time, there is no B involved:

$$G_n(T) = E_n(T = 0) - \frac{V\beta T^4}{12} - \frac{V\gamma T^2}{2} = E_0 - \frac{V\beta T^4}{12} - \frac{V\gamma T^2}{2}.$$

At the critical magnetic field, B_c, the Gibbs free energies are equal, giving

$$G_n(T) = G_s(T) \implies B_c(T)^2 = 8\pi\gamma \left(\frac{(\alpha - \beta)T^4}{12\gamma} - \frac{T^2}{2} + \frac{\Delta}{\gamma} \right)$$

$$= 8\pi\gamma \left(\frac{1}{4}\frac{T^4}{T_c^2} - \frac{T^2}{2} + \frac{T_c^2}{4} \right)$$

$$= 2\pi\gamma T_c^2 \left(\frac{T^4}{T_c^4} - 2\frac{T^2}{T_c^2} + 1 \right)$$

$$= \underbrace{2\pi\gamma T_c^2}_{B_0^2} \left(1 - \frac{T^2}{T_c^2} \right)^2$$

$$\implies \boxed{B_c(T) = B_0 \left(1 - \frac{T^2}{T_c^2} \right)}$$

as desired. Here, $B_0 = T_c\sqrt{2\pi\gamma}$.

(f) Mathematica code:

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In[9]:= Solve[-v*d + a*Tc^4/4 - Tc*a*Tc^3/3 ==
b*Tc^4/4 + g*Tc^2/2 - Tc*(b*Tc^3/3 + g*Tc), d][[1]] //
FullSimplify // Expand

Out[9]= {d -> (g Tc^2)/(2 v) - (a Tc^4)/(12 v) + (b Tc^4)/(12 v)}

In[11]:= (g Tc^2)/(2 v) - (a Tc^4)/(12 v) + (b Tc^4)/(
12 v) /. {Tc -> Sqrt[3*g/(a - b)]} // FullSimplify

Out[11]= (3 g^2)/(4 a v - 4 b v)
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5. Photon gas Carnot cycle.

(a) The work W done in the cycle is simply the area of the parallelogram:

$$\boxed{W = dPdV}$$

(b) Pick the isotherm T. Starting with $dE = đQ + đW$, we find

$$đQ = dE - đW$$

$$= \left.\frac{\partial E}{\partial V}\right|_T dV + PdV$$

$$= \boxed{\left(\left.\frac{\partial E}{\partial V}\right|_T + P \right) dV}$$

(c) The Carnot engine efficiency is

$$\eta = 1 - \frac{T}{T + dT} = \frac{dT}{T + dT} \approx \boxed{\frac{dT}{T}} = \frac{W}{Q} = \boxed{\frac{dP}{\left.\frac{\partial E}{\partial V}\right|_T + P}}$$

(d) With $P = AT^4$, we have

$$\frac{dT}{T} = \frac{4AT^3\,dT}{\left.\frac{\partial E}{\partial V}\right|_T + AT^4}$$

$$\implies \left.\frac{\partial E}{\partial V}\right|_T = 3AT^4 \implies \boxed{E(T,V)} = E(T,0) + 3AT^4V = \boxed{3AT^4V} = 3PV$$

(e) The adiabatic condition requries that $đQ = 0$, so we have

$$dE = đW \implies 3(PdV + VdP) = -PdV \implies \int 4dV/V = -\int 3dP/P \implies \boxed{(PV)^{4/3} = \text{constant}}$$

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6. Irreversible Processes.

(a) Starting with the change in entropy:

$$\Delta S = \Delta S_1 + \Delta S_2 \geq \int_{T_1^0}^{T_f} \frac{đQ_1}{T_1} + \int_{T_2^0}^{T_f} \frac{đQ_2}{T_2} = \int \frac{T_1 - T_2}{T_1 T_2} đQ.$$

Let $đQ = đQ_{12}$ denote the heat flow from 1 to 2. If $T_1 \geq T_2$ then heat flows from 1 to 2 according to the second law, and so $đQ \geq 0$. If $T_1 < T_2$ then heat flows in the opposite direction, and $đQ < 0$. Thus, the product $(T_1 - T_2)d\bar{Q} \geq 0$ for all T_1, T_2. As a result, $\Delta S \geq 0$. At equilibrium, entropy no longer changes, and so S_{final} must be at maximum.

(b) We consider the change in total entropy of the system:

$$\Delta S = \Delta S_{\text{bath}} + \Delta S_{\text{gas}}$$

$$= \Delta S_{\text{gas}} - \frac{1}{T}\Delta E_{\text{gas}} - \frac{1}{T}P\Delta V_{\text{gas}}$$

$$= -\frac{1}{T}\left(\Delta E_{\text{gas}} - T\Delta S_{\text{gas}} - P\Delta V_{\text{gas}}\right)$$

$$= -\frac{1}{T}\Delta G_{\text{gas}}.$$

Since $\Delta S \geq 0$, we must have that $\Delta G \leq 0$. In part (a), we saw an example where "*in a closed system, equilibrium is characterized by the maximum value of entropy S*". In view of this result (or, the second law of thermodymamics), G must minimize, i.e., "*the equilibrium of a gas at fixed T and P is characterized by the minimum of the Gibbs free energy $G = E + PV - TS$*".

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7. Relaxation dynamics.

(a) Since we want to minimize

$$H = U - \mathbf{J} \cdot \mathbf{x},$$

the "first derivative" of $U(\mathbf{x})$ must be equal to $\mathbf{J}$ and the "second derivative" of $U(\mathbf{x})$ must be positive. More precisely, a stable equilibrium is attained whereever $\nabla U = \mathbf{J}$ and the Hessian matrix $D = [\partial^2 U/\partial x_i \partial x_j]$ is positive definite.

(b) Starting with $H = U - J_i x_i$, we take the (total) time derivative and set it negative to ensure that H decreases as the system relaxes:

$$0 < \frac{d}{dt}H$$

$$= \frac{dU}{dt} + \frac{d}{dt}(J_i x_i)$$

$$= \frac{\partial U}{\partial x_i}\dot{x}_i + \cancel{\frac{\partial U}{\partial t}} + J_i \dot{x}_i$$

$$= -\left(\frac{\partial U}{\partial x_i} + J_i\right)\gamma_{ik}\left(\frac{\partial U}{\partial x_k} - J_k\right)$$

$$= -\delta J_i \gamma_{ik} \delta J_k,$$

i.e., that $\delta J_i \gamma_{ik} \delta J_k > 0$. In other words, we require that $\mathbf{\Gamma} = \{\gamma_{ik}\}$ be **positive definite**.

(c) Once again we require that $dG/dt < 0$. This implies (since T is fixed)

$$
\begin{aligned}
0 > \; & \frac{dE}{dt} - \frac{d(J_i x_i)}{dt} - \frac{d(TS)}{dT} \\
= \; & \left(\frac{\partial E}{\partial x_i} - J_i \right) \dot{x}_i - \dot{Q} \\
= \; & -\delta J_i \gamma_{ik} \delta J_k - \delta J_i \theta_i \delta T + \kappa \delta T + \lambda_i \delta J_i \\
= \; &
\end{aligned}
$$

for all $\delta J_i, \delta T$, where repeated indices are sums. Since δJ_i and δT are independent, we may first consider the case where $\delta J_i = 0$, then for all δT we must have $\kappa \delta T < 0$. This implies that $\boxed{\kappa = 0}$. Next, consider $\delta T = 0$. In this case, we must have

$$
\delta J_i \gamma_{ik} \delta J_k > \lambda_i \delta J_i
$$

for all δJ_i. Now what? Is there a way to simplify/reduce this constraint? What we do about θ_i?

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8. The solar system.

(a) The motion and organization of planets is much more ordered than the original dust cloud. However, this does not violate the second law of thermodynamics because during the formation of planets, much of potential energy (due to gravity) among other forms of energy were released into the universe, carrying entropy away. So even though the solar system looks ordered, it is only a part of the larger thermodynamic system (solar system + the rest of the universe) whose total entropy is increased.

(b) The nuclear processes of the sun convert protons to heavier elements such as carbon. However, this further organization does not lead to a reduction in entropy because nuclear fusion releases (less ordered) energy causing an increase in the entropy of the total system (sun + universe).

(c) The evolution of life and intelligence requires even further levels of organization. This is achieved on Earth without violating the second law by evolution is constantly powered by multiple energy sources such as radiation from the Sun, geothermal heat, fossil fuels, etc. Organisms consume these sources of energy and convert them into other forms that are less usable, less ordered.