Thermodynamics

1. *Non-Carnot Engine:* Consider an engine that operates between a set of temperatures $T_{\max} = T_1 > T_2 > T_3 > \cdots > T_n = T_{\min}$. For a subset of these temperatures $\{T_\alpha^+\}$, the engine takes in heat $\{Q_\alpha^+\}$; while at the remaining temperatures $\{T_\beta^-\}$, heat $\{Q_\beta^-\}$ is released. The engine does a net work $W = Q^+ - Q^-$, and its efficiency is given by $\eta = W/Q_+$, where $Q^+ = \sum_\alpha Q_\alpha^+$ and $Q^- = \sum_\beta Q_\beta^-$. Show that this efficiency is less than that of a Carnot engine operating between $T_{\max}$ and $T_{\min}$.

• Using Clausius' theorem,

$$\sum_\alpha \frac{Q_\alpha^+}{T_\alpha} - \sum \frac{Q_\beta^-}{T_\beta} \leq 0, \quad \Longrightarrow \quad \sum_\alpha \frac{Q_\alpha^+}{T_\alpha} \leq \sum \frac{Q_\beta^-}{T_\beta}.$$

Multiplying each term on the left hand side of the inequality by $T_\alpha/T_{\max} \leq 1$ makes its contribution smaller, strengthening the inequality; multiplying each term on the right hand side by $T_\beta/T_{\min} \geq 1$ has a similar effect. Thus

$$\sum_\alpha \frac{Q_\alpha^+}{T_\alpha} \times \frac{T_\alpha}{T_{\max}} \leq \sum \frac{Q_\beta^-}{T_\beta} \times \frac{T_\beta}{T_{\min}}.$$

After factoring out $T_{\max}$ and $T_{\min}$ on the two sides, the sums indicate the total heat taken up or released by the engine, i.e.

$$\frac{Q^+}{T_{\max}} \leq \frac{Q^-}{T_{\min}}, \quad \Longrightarrow \quad 1 - \frac{Q^-}{Q^+} \leq 1 - \frac{T_{\min}}{T_{\max}}, \quad \Longrightarrow \quad \eta = \frac{W}{Q^+} \leq \frac{T_{\max} - T_{\min}}{T_{\max}}.$$

****

2. *Heat exchange between identical bodies:* A collection of n identical bodies, of temperature independent heat capacity C, are initially at temperatures $\{\theta_1, \theta_2, \cdots, \theta_n\}$.

(a) If these bodies are brought into contact such that the only heat exchange is allowed between them, what is the final temperature T_F, and what is the change in entropy.

• If the only heat exchange is between the two bodies,

$$0 = \sum_\alpha Q_\alpha = C \sum_\alpha dT_\alpha.$$

Integrating the above equation from the initial to final state gives

$$\sum_\alpha \theta_\alpha = nT_F \,, \quad \implies \quad T_F = \frac{\sum_\alpha \theta_\alpha}{n} = \overline{\theta} \,,$$

where $\overline{\theta}$ is the mean of the initial temperatures. The overall change in entropy is

$$\Delta S = \sum_\alpha \int_{\theta_\alpha}^{T_F} \frac{dQ_\alpha}{T_\alpha} = C \sum_\alpha \int_{\theta_\alpha}^{T_F} \frac{dT_\alpha}{T_\alpha} = C \sum_\alpha \ln \frac{T_F}{\theta_\alpha} = n \ln \frac{T_F}{\tilde{\theta}} \,,$$

where $\tilde{\theta} \equiv \left(\prod_\alpha \theta_\alpha \right)^{1/n}$ is the geometric mean of the initial temperatures.

(b) What is the final temperature if a Carnot engine is used to transfer heat between the n bodies? What is the amount of work done by the engine in this case?

• With a Carnot engine, the heat transfers are related by

$$0 = dS = \sum_\alpha \frac{dQ_\alpha}{T_\alpha} = C \sum_\alpha \frac{dT_\alpha}{T_\alpha} \,.$$

Integrating the above equation from the initial to final state gives

$$0 = C \sum_\alpha \ln \frac{T_F}{\theta_\alpha} \,, \quad \implies \quad T_F = \left(\prod_\alpha \theta_\alpha \right)^{1/n} \equiv \tilde{\theta} \,.$$

The work done by the Carnot engine is equal to

$$W = C \sum_\alpha \int_{T_F}^{\theta_\alpha} dQ_\alpha = C \sum_\alpha (\theta_\alpha - T_F)$$
$$= nC \left(\overline{\theta} - \tilde{\theta} \right) \geq 0 \,.$$

(c) What is the theoretical maximum temperature T_H to which one of the bodies can be raised at the expense of the other $(n-1)$ bodies? (Any work generated in the process can in principle be stored and reused.) You can leave the answer in the form of an implicit equation for T_H without solving it.

• We can operate multiple Carnot engines to exchange heat amongst the different bodies, storing any work generated (e.g. in frictionless springs). This work can be used to run the engines backwards, operating as refrigerators. During all stages of operation of these Carnot engines, we have

$$S = \sum_{\alpha=1}^n \frac{dQ_\alpha}{T_\alpha} = C \sum_{\alpha=1}^n \frac{dT_\alpha}{T_\alpha} = 0 \,, \quad \implies \quad \prod_{\alpha=1}^n T_\alpha = \prod_{\alpha=1}^n \theta_\alpha \equiv P \,.$$

If at the end of the process no work has been done on the environment, the initial and final heat contents must be the same, i.e.

$$\Delta E = \Delta Q + \Delta W = C \sum_{\alpha=1}^{n} (T_\alpha - \theta_\alpha) = 0 , \quad \Longrightarrow \quad \sum_{\alpha=1}^{n} T_\alpha = \sum_{\alpha=1}^{n} \theta_\alpha \equiv S .$$

If in the final state one body is raised to a temperature T_H, while the remaining bodies are at a temperature T_C, the above identities imply

$$T_H T_C^{n-1} = P \qquad \text{and} \qquad T_H + (n-1)T_C = S .$$

Eliminating T_C between the above equations yields the implicit equation

$$T_H \left(\frac{\sum_{\alpha=1}^{n} \theta_\alpha - T_H}{n-1} \right)^{n-1} = \prod_{\alpha=1}^{n} \theta_\alpha .$$

(d) For the case of $n = 3$, with $\theta_1 = \theta_2 = \theta_H$, and $\theta_3 = \theta_C < \theta_H$, find the explicit solution for $T_H(\theta_H, \theta_C)$.

● For this specific case of three bodies, we obtain the cubic equation

$$T_H(\theta_C + 2\theta_H - T_H)^2 = 4\theta_C \theta_H^2 , \quad \Longrightarrow \quad T_H^3 - 2(\theta_C + 2\theta_H)T_H^2 + (\theta_C + 2\theta_H)^2 T_H - 4\theta_C \theta_H^2 = 0 .$$

Fortunately, we already know that the initial state provides a solution $T_H = \theta_C$ to the cubic equation, enabling us to factor the expression as

$$(T_H - \theta_C) \left[T_H^2 - (\theta_C + 4\theta_H)T_H + 4\theta_H^2 \right] = 0 .$$

Solving the quadratic equation is now straightforward, leading to the solutions

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

and a corresponding

$$T_C = \frac{1}{4} \left[\theta_C \mp \sqrt{\theta_C(\theta_C + 8\theta_H)} \right] .$$

Clearly the plus sign in T_H leads to a negative value of T_c, which is not acceptable, and thus

$$T_H = \frac{1}{2} \left[\theta_C + 4\theta_H - \sqrt{\theta_C(\theta_C + 8\theta_H)} \right] .$$

****

3. *Hard core gas:* A gas obeys the equation of state $P(V - Nb) = Nk_BT$, and has a heat capacity C_V independent of temperature. (N is kept fixed in the following.)

(a) Find the Maxwell relation involving $\partial S/\partial V|_{T,N}$.

• For $dN = 0$,

$$d(E - TS) = -SdT - PdV, \quad \Longrightarrow \quad \left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial P}{\partial T}\right|_{V,N}.$$

(b) By calculating $dE(T, V)$, show that E is a function of T (and N) only.

• Writing dS in terms of dT and dV,

$$dE = TdS - PdV = T\left(\left.\frac{\partial S}{\partial T}\right|_{V,N} dT + \left.\frac{\partial S}{\partial V}\right|_{T,N} dV\right) - PdV.$$

Using the Maxwell relation from part (a), we find

$$dE(T, V) = T\left.\frac{\partial S}{\partial T}\right|_{V,N} dT + \left(T\left.\frac{\partial P}{\partial T}\right|_{V,N} - P\right) dV.$$

But from the equation of state, we get

$$P = \frac{Nk_BT}{(V - Nb)}, \quad \Longrightarrow \quad \left.\frac{\partial P}{\partial T}\right|_{V,N} = \frac{P}{T}, \quad \Longrightarrow \quad dE(T, V) = T\left.\frac{\partial S}{\partial T}\right|_{V,N} dT,$$

i.e. $E(T, N, V) = E(T, N)$ does not depend on V.

(c) Show that $\gamma \equiv C_P/C_V = 1 + Nk_B/C_V$ (independent of T and V).

• The hear capacity is

$$C_P = \left.\frac{\partial Q}{\partial T}\right|_P = \left.\frac{\partial E + PV}{\partial T}\right|_P = \left.\frac{\partial E}{\partial T}\right|_P + P\left.\frac{\partial V}{\partial T}\right|_P.$$

But, since $E = E(T)$ only,

$$\left.\frac{\partial E}{\partial T}\right|_P = \left.\frac{\partial E}{\partial T}\right|_V = C_V,$$

and from the equation of state we get

$$\left.\frac{\partial V}{\partial T}\right|_P = \frac{Nk_B}{P}, \quad \Longrightarrow \quad C_P = C_V + Nk_B, \quad \Longrightarrow \quad \gamma = 1 + \frac{Nk_B}{C_V},$$

which is independent of T, since C_V is independent of temperature. The independence of C_V from V also follows from part (a).

(d) By writing an expression for $E(P, V)$, or otherwise, show that an adiabatic change satisfies the equation $P(V - Nb)^\gamma =$constant.

- Using the equation of state, we have

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

The adiabatic condition, $dQ = dE + PdV = 0$, can now be written as

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

Dividing by $C_V P(V - Nb)/(Nk_B)$ yields

$$\frac{dP}{P} + \gamma \frac{d(V - Nb)}{(V - Nb)} = 0, \quad \Longrightarrow \quad \ln \left[P(V - Nb)^\gamma \right] = constant.$$

****

4. *Superconducting transition:* Many metals become superconductors at low temperatures T, and magnetic fields B. The heat capacities of the two phases at zero magnetic field are approximately given by

$$\begin{cases} C_s(T) = V\alpha T^3 & \text{in the superconducting phase} \\ C_n(T) = V \left[\beta T^3 + \gamma T \right] & \text{in the normal phase} \end{cases},$$

where V is the volume, and $\{\alpha, \beta, \gamma\}$ are constants. (There is no appreciable change in volume at this transition, and mechanical work can be ignored throughout this problem.)

(a) Calculate the entropies $S_s(T)$ and $S_n(T)$ of the two phases at zero field, using the third law of thermodynamics.

- Finite temperature entropies are obtained by integrating $dS = đQ/T$, starting from $S(T = 0) = 0$. Using the heat capacities to obtain the heat inputs, we find

$$\begin{cases} C_s = V\alpha T^3 = T\dfrac{dS_s}{dT}, & \Longrightarrow \quad S_s = V\dfrac{\alpha T^3}{3}, \\ C_n = V \left[\beta T^3 + \gamma T \right] = T\dfrac{dS_n}{dT}, & \Longrightarrow \quad S_n = V \left[\dfrac{\beta T^3}{3} + \gamma T \right] \end{cases}.$$

(b) Experiments indicate that there is no latent heat $(L = 0)$ for the transition between the normal and superconducting phases at zero field. Use this information to obtain the transition temperature T_c, as a function of α, β, and γ.

• The Latent hear for the transition is related to the difference in entropies, and thus

$$L = T_c \left(S_n(T_c) - S_s(T_c) \right) = 0.$$

Using the entropies calculated in the previous part, we obtain

$$\frac{\alpha T_c^3}{3} = \frac{\beta T_c^3}{3} + \gamma T_c, \quad \Longrightarrow \quad T_c = \sqrt{\frac{3\gamma}{\alpha - \beta}}.$$

(c) At zero temperature, the electrons in the superconductor form bound Cooper pairs. As a result, the internal energy of the superconductor is reduced by an amount $V\Delta$, i.e. $E_n(T = 0) = E_0$ and $E_s(T = 0) = E_0 - V\Delta$ for the metal and superconductor, respectively. Calculate the internal energies of both phases at finite temperatures.

• Since $dE = TdS + BdM + \mu dN$, for $dN = 0$, and $B = 0$, we have $dE = TdS = CdT$. Integrating the given expressions for heat capacity, and starting with the internal energies E_0 and $E_0 - V\Delta$ at $T = 0$, yields

$$\begin{cases} E_s(T) = E_0 + V \left[-\Delta + \frac{\alpha}{4} T^4 \right] \\ E_n(T) = E_0 + V \left[\frac{\beta}{4} T^4 + \frac{\gamma}{2} T^2 \right] \end{cases}.$$

(d) By comparing the Gibbs free energies (or chemical potentials) in the two phases, obtain an expression for the energy gap Δ in terms of α, β, and γ.

• The Gibbs free energy $G = E - TS - BM = \mu N$ can be calculated for $B = 0$ in each phase, using the results obtained before, as

$$\begin{cases} G_s(T) = E_0 + V \left[-\Delta + \frac{\alpha}{4} T^4 \right] - TV \frac{\alpha}{3} T^3 = E_0 - V \left[\Delta + \frac{\alpha}{12} T^4 \right] \\ G_n(T) = E_0 + V \left[\frac{\beta}{4} T^4 + \frac{\gamma}{2} T^2 \right] - TV \left[\frac{\beta}{3} T^3 + \gamma T \right] = E_0 - V \left[\frac{\beta}{12} T^4 + \frac{\gamma}{2} T^2 \right] \end{cases}.$$

At the transition point, the chemical potentials (and hence the Gibbs free energies) must be equal, leading to

$$\Delta + \frac{\alpha}{12} T_c^4 = \frac{\beta}{12} T_c^4 + \frac{\gamma}{2} T_c^2, \quad \Longrightarrow \quad \Delta = \frac{\gamma}{2} T_c^2 - \frac{\alpha - \beta}{12} T_c^4.$$

Using the value of $T_c = \sqrt{3\gamma/(\alpha - \beta)}$, we obtain

$$\Delta = \frac{3}{4} \frac{\gamma^2}{\alpha - \beta}.$$

(e) In the presence of a magnetic field B, inclusion of magnetic work results in $dE = TdS + BdM + \mu dN$, where M is the magnetization. The superconducting phase is a perfect diamagnet, expelling the magnetic field from its interior, such that $M_s = -VB/(4\pi)$ in appropriate units. The normal metal can be regarded as approximately non-magnetic, with $M_n = 0$. Use this information, in conjunction with previous results, to show that the superconducting phase becomes normal for magnetic fields larger than

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

giving an expression for B_0.

• Since $dG = -SdT - MdB + \mu dN$, we have to add the integral of $-MdB$ to the Gibbs free energies calculated in the previous section for $B = 0$. There is no change in the metallic phase since $M_n = 0$, while in the superconducting phase there is an additional contribution of $-\int M_s dB = (V/4\pi) \int B dB = (V/8\pi) B^2$. Hence the Gibbs free energies at finite field are

$$\begin{cases} G_s(T, B) = E_0 - V \left[\Delta + \frac{\alpha}{12} T^4 \right] + V \frac{B^2}{8\pi} \\ G_n(T, B) = E_0 - V \left[\frac{\beta}{12} T^4 + \frac{\gamma}{2} T^2 \right] \end{cases}.$$

Equating the Gibbs free energies gives a critical magnetic field

$$\frac{B_c^2}{8\pi} = \Delta - \frac{\gamma}{2} T^2 + \frac{\alpha - \beta}{12} T^4 = \frac{3}{4} \frac{\gamma^2}{\alpha - \beta} - \frac{\gamma}{2} T^2 + \frac{\alpha - \beta}{12} T^4$$

$$= \frac{\alpha - \beta}{12} \left[\left(\frac{3\gamma}{\alpha - \beta} \right)^2 - \frac{6\gamma T^2}{\alpha - \beta} + T^4 \right] = \frac{\alpha - \beta}{12} \left(T_c^2 - T^2 \right)^2,$$

where we have used the values of Δ and T_c obtained before. Taking the square root of the above expression gives

$$B_c = B_0 \left(1 - \frac{T^2}{T_c^2} \right), \quad \text{where} \quad B_0 = \sqrt{\frac{2\pi(\alpha - \beta)}{3}} T_c^2 = \sqrt{\frac{6\pi\gamma^2}{\alpha - \beta}} = T_c \sqrt{2\pi\gamma}.$$

5. *Photon gas Carnot cycle:* The aim of this problem is to obtain the blackbody radiation relation, $E(T, V) \propto V T^4$, starting from the equation of state, by performing an infinitesimal Carnot cycle on the photon gas.
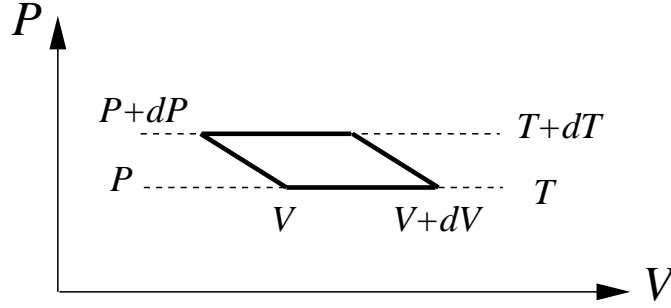
(a) Express the work done, W, in the above cycle, in terms of dV and dP.

• Ignoring higher order terms, net work is the area of the cycle, given by $W = dP dV$.

(b) Express the heat absorbed, Q, in expanding the gas *along an isotherm*, in terms of P, dV, and an appropriate derivative of $E(T, V)$.

• Applying the first law, the heat absorbed is

$$Q = dE + PdV = \left[\left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV + PdV \right]_{\text{isotherm}} = \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] dV.$$

(c) Using the efficiency of the Carnot cycle, relate the above expressions for W and Q to T and dT.

• The efficiency of the Carnot cycle ($\eta = dT/T$) is here calculated as

$$\eta = \frac{W}{Q} = \frac{dP}{[(\partial E/\partial V)_T + P]} = \frac{dT}{T}.$$

(d) Observations indicate that the pressure of the photon gas is given by $P = AT^4$, where $A = \pi^2 k_B^4 / 45 \, (\hbar c)^3$ is a constant. Use this information to obtain $E(T, V)$, assuming $E(T, 0) = 0$.

• From the result of part (c) and the relation $P = AT^4$,

$$T \frac{\partial P}{\partial T} = 4AT^4 = \left(\frac{\partial E}{\partial V} \right)_T + AT^4, \quad \text{or} \quad \left(\frac{\partial E}{\partial V} \right)_T = 3AT^4,$$

so that

$$E = 3AVT^4.$$

(e) Find the relation describing the *adiabatic paths* in the above cycle.

- Adiabatic curves are given by $dQ = 0$, or

$$0 = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + P dV = 3V dP + 4P dV,$$

i.e.

$$PV^{4/3} = \text{constant.}$$

****

6. (Optional) *Irreversible Processes:*

(a) Consider two substances, initially at temperatures T_1^0 and T_2^0, coming to equilibrium at a final temperature T_f through heat exchange. By relating the direction of heat flow to the temperature difference, show that the change in the total entropy, which can be written as

$$\Delta S = \Delta S_1 + \Delta S_2 \geq \int_{T_1^0}^{T_f} \frac{dQ_1}{T_1} + \int_{T_2^0}^{T_f} \frac{dQ_2}{T_2} = \int \frac{T_1 - T_2}{T_1 T_2} dQ,$$

must be positive. This is an example of the more general condition that "*in a closed system, equilibrium is characterized by the maximum value of entropy S.*"

- Defining the heat flow from substance 1 to 2 as, $dQ_{1 \to 2}$, we get,

$$\Delta S = \Delta S_1 + \Delta S_2 \geq \int_{T_1^0}^{T_f} \frac{dQ_1}{T_1} + \int_{T_2^0}^{T_f} \frac{dQ_2}{T_2} = \int \frac{T_1 - T_2}{T_1 T_2} dQ_{1 \to 2}.$$

But according to Clausius' statement of the second law $dQ_{1 \to 2} > 0$, if $T_1 > T_2$ and $dQ_{1 \to 2} < 0$, if $T_1 < T_2$. Hence, $(T_1 - T_2)dQ_{1 \to 2} \geq 0$, resulting in

$$\Delta S \geq \int \frac{T_1 - T_2}{T_1 T_2} dQ_{1 \to 2} \geq 0.$$

(b) Now consider a gas with adjustable volume V, and diathermal walls, embedded in a heat bath of constant temperature T, *and* fixed pressure P. The change in the entropy of the bath is given by

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

By considering the change in entropy of the combined system establish that "*the equilibrium of a gas at fixed T and P is characterized by the minimum of the Gibbs free energy $G = E + PV - TS$.*"

- The total change in entropy of the whole system is,

$$\Delta S = \Delta S_{\text{bath}} + \Delta S_{\text{gas}} = -\frac{1}{T}(\Delta E_{\text{gas}} + P\Delta V_{\text{gas}} - T\Delta S_{\text{gas}}) = -\frac{1}{T}\Delta G_{\text{gas}}.$$

By the second law of thermodynamics, all processes must satisfy,

$$-\frac{1}{T}\Delta G_{\text{gas}} \geq 0 \quad \Leftrightarrow \quad \Delta G_{\text{gas}} \leq 0,$$

that is, all processes that occur can only lower the Gibbs free energy of the gas. Therefore the equillibrium of a gas in contact with a heat bath of constant T and P is established at the point of minimum Gibbs free energy, i.e. when the Gibbs free energy cannot be lowered any more.

<div align="center">********</div>

7. *Relaxation dynamics:* Consider a mechanical system described by displacements $\mathbf{x} = \{x_i\}$ and potential energy $U(\mathbf{x})$. When subject to conjugate external forces $\mathbf{J} = \{J_i\}$, a stable equilibrium is obtained by minimizing $H = U - \mathbf{J} \cdot \mathbf{x}$.

(a) What are the conditions on the first and second derivatives of $U(\mathbf{x})$ at the equilibrium point $\mathbf{x}_0$?

- Requiring that $\mathbf{x}_0$ is a minimum of $H = U - \mathbf{J} \cdot \mathbf{x}$ leads to $\frac{\partial U}{\partial x_i} = J_i$, at this point. Furthermore the matrix of second derivatives $\frac{\partial^2 U}{\partial x_i \partial x_j}$ must be positive definite at $\mathbf{x}_0$.

Following a small displacement away from equilibrium to $\delta\mathbf{x} = \mathbf{x} - \mathbf{x}_0$, (in linear response) the displacements relax back to equilibrium with 'velocities' $v_i = \dot{x}_i = -\sum_k \gamma_{ik}\delta J_k$; where $\boldsymbol{\Gamma} \equiv \{\gamma_{ik}\}$ are *kinetic coefficients*, and $\delta J_k = \frac{\partial U}{\partial x_k} - J_k$ is the difference between internal and external force.

(b) Assuming dissipative relaxation always proceeds such that H is decreased; what is the constraint on $\boldsymbol{\Gamma} \equiv \{\gamma_{ik}\}$?

• Under the proposed relaxation dynamics the time variation of H is given by

$$\frac{dH}{dt} = \sum_i \left[\frac{\partial U}{\partial x_i} - J_i\right]\dot{x}_i = \sum_i \delta J_i\left(-\sum_k \gamma_{ik}\delta J_k\right) = -\delta \mathbf{J}\cdot\mathbf{\Gamma}\cdot\delta\mathbf{J} \leq 0\,,$$

i.e. the matrix $\mathbf{\Gamma}$ has to be positive definite.

The above discussion can be extended to a thermodynamic system, in which case internal energy can change by both mechanical work and heat. At a temperature T, equilibrium is obtained by minimizing $G = E - \mathbf{J}\cdot\mathbf{x} - TS$. With the entropy S as an additional coordinate,

$$\dot{x}_i = -\sum_k \gamma_{ik}\delta J_k - \theta_i\ \delta T,$$

with $\mathbf{\Theta} = \{\theta_i\}$ as kinetic coefficients relating velocities to temperature differences in the linear regime. Similarly the heat flux into the system can be written as

$$\dot{Q} = T\dot{S} = -\kappa\delta T - \sum_i \lambda_i\delta J_i.$$

(c) What is the stability constraint for the parameters $\mathbf{\Gamma}$, $\mathbf{\Theta}$, $\mathbf{\Lambda} = \{\lambda_i\}$, and κ?

• The thermodynamic generalization of displacement is the entropy S, whose flux obeys

$$\dot{S} = -\frac{\kappa}{T}\delta T - \sum_i \frac{\lambda_i}{T}\delta J_i.$$

The mechanical stability matrix $\mathbf{\Gamma}$ must thus be generalized to include the column vector $\mathbf{\Theta}$ to the top-right, the row vector $\mathbf{\Lambda}/T$ at bottom-left, and κ/T at the bottom right corner. This generalized matrix should be positive definite.

****

8. (Optional) *The solar system* originated from a dilute gas of particles, sufficiently separated from other such clouds to be regarded as an isolated system. Under the action of gravity the particles coalesced to form the sun and planets.

(a) The motion and organization of planets is much more ordered than the original dust cloud. Why does this not violate the second law of thermodynamics?

• The formation of planets is due to the gravitational interaction. Because of the attractive nature of this interaction, the original dust cloud with uniform density has in fact lower entropy. Clumping of the uniform density leads to higher entropy. Of course the

gravitational potential energy is converted into kinetic energy in the process. Ultimately the kinetic energy of falling particles is released in the form of photons which carry away a lot of entropy.

(b) The nuclear processes of the sun convert protons to heavier elements such as carbon. Does this further organization lead to a reduction in entropy?

• Again the process of formation of heavier elements is accompanied by the release of large amounts of energy which are carry away by photons. The entropy carry away by these photons is more than enough to compensate any ordering associated with the packing of nucleons into heavier nuclei.

(c) The evolution of life and intelligence requires even further levels of organization. How is this achieved on earth without violating the second law?

• Once more there is usage of energy by the organisms that converts more ordered forms of energy to less ordered ones.

****