General Physics II: Tutorial Material

Lecture 14 (Chapter 11 – Heat transfer and Review)

1) Black body radiation: A black body is an object at equilibrium with the radiation it emits. This radiation is characterized by the fact that the internal energy density depends only on the temperature at thermal equilibrium. The internal energy of this radiation is given by:

$$E_{int}(S,V) = \frac{3}{4}\left(\frac{3c}{16\sigma}\right)^{1/3} S^{4/3}V^{-1/3} \tag{1}$$

where sigma is the Stefan Boltzmann constant (see lecture).

a) Determine the free energy $F(T,V)$ of this radiation.

b) Show that the internal energy $U(S,V)$ of the radiation can be obtained by performing an inverse Legendre transformation on the free energy $F(T,V)$ (i.e. $E_{int}(S,V) = F + ST$).

c) Find expressions for $P(T,V)$ and $P(S,V)$ for the radiation pressure.

Solution:

a) We can obtain the temperature of the black body via

$$T(S,V) = \frac{\partial E_{int}(S,V)}{\partial S} = \left(\frac{3c}{16\sigma}\right)^{1/3} S^{1/3}V^{-1/3} \tag{2}$$

When inverting this relation we obtain the radiation entropy $S(T,V)$ as a function of T and V:

$$S(T,V) = \left(\frac{16\sigma}{3c}\right) T^3 V \tag{3}$$

When substituting this result into the expression for the internal energy of the radiation E_{int}, we find: $E_{int} = 4\sigma/cT^4V$.
The free energy can be obtained from E_{int} and the above expressions for T and S via

$$F = E_{int} - TS = -\frac{4\sigma}{3c}T^4V \tag{4}$$

b) We can estimate the entropy for the black body radiation from the free energy F

$$S(T,V) = -\frac{\partial F}{\partial T} = \frac{16\sigma}{3c}T^3V \tag{5}$$

When inverting this relation, we obtain the radiation temperature $T(S,V)$, i.e.:

$$T(S,V) = \left(\frac{3c}{16\sigma}\right)^{1/3} S^{1/3}V^{-1/3} \tag{6}$$

When substituting for T in the radiation free energy $F(T,V)$, we find:

$$F = -\frac{1}{4}\left(\frac{3c}{16\sigma}\right)^{1/3} S^{4/3}V^{-1/3} \tag{7}$$

c) According the the definition in Lecture 8, the black body radiation pressure $P(S,V)$ can be derived from the internal energy via:

$$P(S,V) = -\frac{E_{int}(S,V)}{\partial V} = \frac{1}{4}\left(\frac{3c}{16\sigma}\right)^{1/3} S^{4/3}V^{-4/3} \tag{8}$$

And the radiation pressure $P(T,V)$, i.e. P is a function of T and V, can be derived from the free energy F via:

$$P(T,V) = -\frac{\partial F(T,V)}{\partial V} = \frac{4\sigma}{3c}T^4 \tag{9}$$

2) Exercise taken from a previous exam:
We consider a system of two solid bodies, A and B, with their masses, m_A and m_B, and specific heats per mass, c_A and c_B, respectively. And their initial absolute temperatures are T_A and T_B. Now the two bodies are put together under thermal contact while the system is thermally isolated from the environment.

a) Using the 1^{st} law of thermodynamics, calculate the temperature T_f, when the system has reached thermal equilibrium.

b) Show that T_f is always in between T_A and T_B.

c) Calculate the entropy changes for A and B, ΔS_A and ΔS_B, between the initial and the final thermal equilibrium states.

d) From ΔS_A and ΔS_B obtained above, show that the total entropy change, $\Delta S_A + \Delta S_B$, is always ≥ 0.

Solution:

a) The system consisting of the two blocks A and B is thermally isolated and undergoes no deformation during the process. So, from the first law we know that $\Delta E_{int} = 0$. Since A and B are subsystems, $\Delta E_{int} = E_{int,A} + E_{int,B}$. The work on each subsystem is zero, so that in the end $Q_A = -Q_B$. The heat changes are given by $Q_A = m_A c_A (T_f - T_A)$ and $Q_B = m_B c_B (T_f - T_B)$, respectively. We can hence write

$$m_A c_A (T_f - T_A) + m_B c_B (T_f - T_B) = 0. \tag{10}$$

This leads to

$$T_f = \frac{m_A c_A T_A + m_B c_B T_B}{m_A c_A + m_B c_B} \tag{11}$$

b) By introducing $T_A - T_B = \Delta T$, T_f can be written as

$$T_f = T_A - \frac{m_B c_B \Delta T}{m_A c_A + m_B c_B} = T_B + \frac{m_A c_A \Delta T}{m_A c_A + m_B c_B} \tag{12}$$

where clearly

$$0 < \frac{m_B c_B}{m_A c_A + m_B c_B} < 1 \quad \text{and} \quad 0 < \frac{m_A c_A}{m_A c_A + m_B c_B} < 1 \tag{13}$$

Thus, if $T_A - T_B = \Delta T > 0$, $T_f > T_B$ and $T_f < T_A$. And if $T_A - T_B = \Delta T < 0$, $T_A < T_B$ and $T_f < T_B$, i.e. T_f is always in between T_A and T_B.

c) The conductive heat transfer occuring when the two blocks come into direct contact is an irreversible process, since their temperatures are different and there is a jump in T at the boundary. However, when considering each block separately, we can calculate the heat transfer coming from the other block as if it were reversible, by viewing the other block as a heat reservoir and supposing that the heat transfer occurs in a quasi-static fashion. Using $dS = dQ/T = mc \cdot dT/T$ (where dQ is the heat flowing to or from the other block), we then get

$$\Delta S_A = \int_{T_A}^{T_f} \frac{m_A c_A dT}{T} = m_A c_A \ln \frac{T_f}{T_A} \quad \text{and} \quad \Delta S_B = \int_{T_B}^{T_f} \frac{m_B c_B dT}{T} = m_B c_B \ln \frac{T_f}{T_B} \tag{14}$$

Bonus: The formal justification for why we can compute the transfer in each block as if it were reversible is similar to what was done in previous exercises, namely to replace the irreversible process that we can't deal with by a reversible one that reaches the same final state. It goes as follows: focus on e.g. the block at lower temperature. Rather than coming into direct contact with another finite block which has a higher temperature, consider that it instead comes into contact with a sequence of thermal baths at increasing temperatures. At each step of this procedure, the temperature difference is arbitrarily small and the transfer can thus be considered reversible. At each step, an amount of entropy $dS = dQ/T$ is transfered, where T is the temperature of the bath. Once the block reaches T_f, the total entropy transfered is given by the sum of these dS, which results in the integrals written above.

d) The total change of entropy is given by $\Delta S_{tot} = \Delta S_A + \Delta S_B$. By introducing $x = T_B/T_A$, where the range of x is from 0 to ∞,

$$T_f = \frac{m_A c_A + m_B c_B x}{m_A c_A + m_B c_B} T_A = \frac{m_A c_A + m_B c_B x}{(m_A c_A + m_B c_B)x} T_B \tag{15}$$

thus

$$\frac{T_f}{T_A} = \frac{m_A c_A + m_B c_B x}{m_A c_A + m_B c_B} \quad \text{and} \quad \frac{T_f}{T_B} = \frac{m_A c_A + m_B c_B x}{(m_A c_A + m_B c_B)x} \tag{16}$$

and ΔS_{tot} can be written as

$$\Delta S_{tot} = (m_A c_A + m_B c_B) \ln \frac{m_A c_A + m_B c_B x}{m_A c_A + m_B c_B} - m_B c_B \ln x. \tag{17}$$

At $x = 1$, i.e. $T_A = T_B = T_f$, $\Delta S_{tot} = 0$, which makes sense: since if there is no temperature difference between the blocks, they are already in thermal equilibrium and nothing happens.

By taking derivative of ΔS_{tot} respect to x, we obtain

$$\frac{d\Delta S_{tot}}{dx} = \frac{m_A c_A m_B c_B (x-1)}{(m_A c_A + m_B c_B x)x} \tag{18}$$

leading to $d\Delta S_{tot}/dx < 0$ for $x < 1$ and $d\Delta S_{tot}/dx > 0$ for $x > 1$, i.e. from $x = 0$ to 1, ΔS_{tot} is monotonically decreasing until it reaches 0 at $x = 1$, then monotonically increasing from $x = 1$ to ∞. Therefore $\Delta S \geq 0$.

Note that as soon as $T_A \neq T_B$, $\Delta S > 0$ for the whole system (both blocks). Since the system was thermally isolated, this implies that entropy was produced within the system, which shows that the process was indeed irreversible.

3) Exercise taken from a last year's exam: Atkinson Cycle

James Atkinson was a British engineer who designed several combustion engines. The Atkinson cycle is a modification of the Otto cycle intended to improve its efficiency. The trade-off in achieving higher efficiency is a decrease in the work performed per cycle. The idealized Atkinson cycle consists of the following reversible processes

- 1 → 2: adiabatic compression
- 2 → 3: isochoric heating
- 3 → 4: isobaric expansion
- 4 → 5: adiabatic expansion
- 5 → 6: isochoric cooling
- 6 → 1: isobaric cooling

Assume that the cycle is operated on an ideal gas. The following physical quantities that characterize the cycle are assumed to be known: volumes V_1, V_2, and V_6, pressure P_3 and P_5, temperature T_5 and the number of moles n of the gas. Analyze this cycle by answering the following questions:

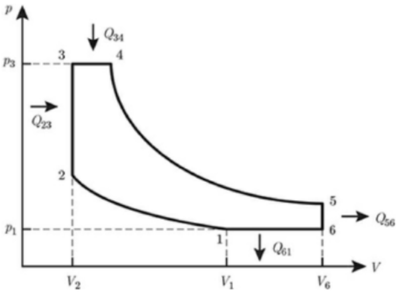
a) Draw the PV diagram of the Atkinson cycle.

b) In which subprocesses is the (reversible) entropy change positive and in which negative? Note that it can be helpful to draw the TS diagram. Why is a negative entropy change not violating the second law?

c) Now suppose that the adiabatic expansion process (4 to 5) is replaced by an isothermal expansion process at constant temperature T_4, and assume to have a van der Waals gas instead of ideal gas, with $P = \frac{nRT}{V-nb} - a\frac{n^2}{V^2}$ and with $E_{int} = C_V T - a\frac{n^2}{V}$. Compute the work done in this process, heat transfer and its entropy change - all quantities as a function of V_4, V_5, and T_4. Also indicate whether the heat transfer and the change in entropy is positive or negative.

Solution:

a)



There is no entropy change during the adiabatic processes, as $dQ = 0$.

b)
Isochoric processes:

$$\Delta S_{23} = \int_{S_2}^{S_3} dS = nC_V \int_{T_2}^{T_3} \frac{dT}{T} = nC_V \ln\left(\frac{T_3}{T_2}\right) \tag{19}$$

$$\Delta S_{56} = \int_{S_5}^{S_6} dS = nC_V \int_{T_5}^{T_6} \frac{dT}{T} = nC_V \ln\left(\frac{T_6}{T_5}\right) \tag{20}$$

Since $T_3 > T_2$, ΔS_{23} is positive, whereas ΔS_{56} is negative since $T_6 < T_5$.

Isobaric processes:

$$\Delta S_{34} = \int_{S_3}^{S_4} dS = nC_P \int_{T_3}^{T_4} \frac{dT}{T} = nC_P \ln\left(\frac{T_4}{T_3}\right) \tag{21}$$

$$\Delta S_{61} = \int_{S_6}^{S_1} dS = nC_P \int_{T_6}^{T_1} \frac{dT}{T} = nC_P \ln\left(\frac{T_1}{T_6}\right) \tag{22}$$

Since $T_4 > T_3$, ΔS_{34} is positive, whereas ΔS_{61} is negative since $T_1 < T_6$.

A negative entropy change in reversible processes is solely due to heat exchange with the environment. The second law states that for isolated/adiabatic systems, i.e. with no heat exchange with the environment, the entropy cannot decrease $dS \geq 0$ (due to entropy production within a system). However, in this exercise, we are not considering an isolated/adiabatic system, thus, the entropy change can be negative.

c)

$$W_{45} = \int_{V_4}^{V_5} PdV = \int_{V_4}^{V_5} \left(\frac{nRT_4}{V - nb} - a\frac{n^2}{V^2}\right) dV \tag{23}$$

Solving the integrals yields:

$$W_{45} = nRT_4 \ln\left(\frac{V_5 - nb}{V_4 - nb}\right) - n^2 a \left(\frac{1}{V_4} - \frac{1}{V_5}\right) \tag{24}$$

The change in internal energy is given by (note that the $C_V \Delta T$ term is zero due to the isothermal process):

$$\Delta E_{int,45} = E_{int,5} - E_{int,4} = n^2 a \left(\frac{1}{V_4} - \frac{1}{V_5}\right) \tag{25}$$

Applying the first law, we obtain for the heat transfer:

$$\begin{aligned} Q_{45} &= \Delta E_{int,45} + W_{45} && (26)\\ &= n^2 a \left(\frac{1}{V_4} - \frac{1}{V_5}\right) + nRT_4 \ln\left(\frac{V_5 - nb}{V_4 - nb}\right) - n^2 a \left(\frac{1}{V_4} - \frac{1}{V_5}\right) && (27)\\ &= nRT_4 \ln\left(\frac{V_5 - nb}{V_4 - nb}\right) > 0, && (28) \end{aligned}$$

which is positive, i.e. heat is added to system as expected for an isothermal expansion process.

We can also express the heat Q via:

$$Q_{45} = \int_4^5 TdS = T_4 \int_{S_4}^{S_5} dS = T_4 \Delta S_{45} \tag{29}$$

Solving for ΔS_{45}, we obtain the entropy change:

$$\Delta S_{45} = \frac{Q_{45}}{T_4} = nR \ln\left(\frac{V_5 - nb}{V_4 - nb}\right) > 0 \tag{30}$$

This means the entropy is increasing during a reversible isothermal expansion process.

To practice a bit more TD potentials:

4) To practice a bit more TD potentials: Pressure in a Soap Bubble: A soap bubble is a system consisting of two subsystems. Subsystem (f) is the thin film and the subsystem (g) is the gas enclosed inside the film. The surrounding air is a thermal bath. The equilibrium is characterized by the minimum of the free energy F of the system. The differential of the free energy dF reads:

$$dF = -(S_g + S_f)dT + 2\gamma dA - (P - P_0)dV, \tag{31}$$

where a is the surface area of the soap film and V the volume of the bubble. The parameter γ is called the surface tension. It characterizes the interactions at the interface between the liquid and the air. Since the soap film has two such interfaces, there is a factor 2 in front of the parameter γ. The surface tension γ is an intensive variable that plays an analogous role for a surfacic system as the pressure P for a volumic system. However, the force due to pressure of a gas is exerted outwards whereas the force due to the surface tension is exerted inwards. This is the reason why the signs of the corresponding two terms in dF differ. The term $P - P_0$ is the pressure difference between the Pressure P inside the bubble and the atmospheric pressure P_0. Consider the bubble to be a sphere of radius r and show that

$$P - P_0 = \frac{4\gamma}{r} \tag{32}$$

Solution:

We know from the lecture that the equilibrium state of a system coupled to a thermal bath is characterized by the minimum of the free energy F, which translates mathematically to $dF = 0$. Since the surrounding air is a thermal bath, the temperature is constant, i.e. $dT = 0$, so that the variation of F reduces to

$$dF = 2\gamma dA - (P - P_0)dV, \tag{33}$$

For a spherical bubble, the area differential is given by:

$$dA = 4\pi(r + dr)^2 - 4\pi r^2 = 4\pi(2rdr + dr^2) \approx 8\pi r dr, \tag{34}$$

where we neglect the second-order term in dr^2. Equivalently, we can get the differential directly from the derivative of the area $\frac{d}{dr}\left(4\pi r^2\right) = 8\pi r \implies dA = 8\pi r dr$. The volume differential is given by:

$$dV = \frac{4\pi}{3}(r + dr)^3 - \frac{4\pi}{3}r^3 = \frac{4\pi}{3}(3r^2dr + 3rdr^2 + dr^3) \approx 4\pi r^2 dr, \tag{35}$$

where we neglect the second-order term in dr^2 and the third-order term in dr^3. Again, using the derivative instead we immediately get $\frac{d}{dr}\left(\frac{4}{3}\pi r^3\right) = 4\pi r^2 \implies dV = 4\pi r^2 dr$.
At equilibrium, the free energy F is minimized, thus,

$$\begin{aligned} dF &= 16\pi\gamma r dr - 4\pi(P - P_0)r^2 dr & (36)\\ &= \left(16\pi\gamma r - 4\pi(P - P_0)r^2\right) dr \overset{!}{=} 0, & (37)\end{aligned}$$

which implies that the term in parentheses must vanish. Setting it to 0 and rearranging yields the result,

$$P - P_0 = \frac{4\gamma}{r}. \tag{38}$$

5) Gibbs-Helmholtz equations: Show that

a)

$$E_{\text{int}}(S, V) = -T^2 \frac{\partial}{\partial T}\left(\frac{F(T, V)}{T}\right) \tag{39}$$

where $T = T(S, V)$ is to be understood as a function of S and V.

b)

$$H(S, P) = -T^2 \frac{\partial}{\partial T}\left(\frac{G(T, P)}{T}\right) \tag{40}$$

where $T = T(S, P)$ is to be understood as a function of S and P.

Solution:

a) The internal energy is related to the free energy F and expressed in terms of the state variables S and V as

$$E_{\text{int}}(S,V) = F(T,V) + TS \tag{41}$$

Using the definition $S = -\frac{\partial F}{\partial T}$ (see lecture notes) and the chain rule, it can be recast as:

$$\begin{aligned} E_{\text{int}}(S,V) &= F(T,V) - T\frac{\partial F(T,V)}{\partial T} \\ &= -T^2 \frac{\partial}{\partial T}\left(\frac{F(T,V)}{T}\right) \end{aligned} \tag{42}$$

b) Likewise, the enthalpy H is related to the Gibbs free energy G and expressed in terms of the state variables S and P as

$$H(S,P) = G(T,P) + TS \tag{43}$$

Using the definition $S = -\frac{\partial G}{\partial T}$ (see lecture notes), and the chain rule, it can be recast as:

$$\begin{aligned} H(S,P) &= G(T,P) - T\frac{\partial G(T,P)}{\partial T} \\ &= -T^2 \frac{\partial}{\partial T}\left(\frac{G(T,P)}{T}\right) \end{aligned} \tag{44}$$