# PHYS 427 - Thermal and Statistical Physics - Discussion 05 - Solutions

1. **Carnot's theorem**: A heat engine is a device that turns heat into mechanical work. More precisely, it takes energy from a large high-temperature reservoir in the form of heat, converts some of that energy into useful mechanical work, and deposits the rest into a large low-temperature reservoir as heat.

   A "good" heat engine is one that converts a lot of the input energy into work. Therefore, the efficiency $\eta$ of a heat engine is defined as the amount of work it produces divided by the amount of heat it takes in.

   In this problem, you will prove Carnot's theorem, which places a fundamental maximum limit on $\eta$, *no matter what the heat engine is made of.*

   Without losing any generality, we can assume that the heat engine operates *cyclically*. During one cycle of the engine, it extracts an amount of energy $Q_H$ from the hot reservoir in the form of heat, produces an amount $W$ of mechanical work, and deposits energy $Q_C$ into the cold reservoir as heat. At the end of the cycle, the engine itself returns to its exact initial state. The reservoirs are very large, so that their temperatures $T_H$ and $T_C$ do not change.

   (a) Apply the first law of thermodynamics ($dU = \dbar Q + \dbar W$) to the engine itself (not including the reservoirs). Integrate over a full cycle to show that $\eta \leq 1$. This is sometimes summarized by saying "you can't win" in the game of thermodynamics. (This isn't Carnot's theorem yet, keep going!)

   (b) Assume that the number of particles in the hot reservoir is fixed[1], but allow for the possibility that it can expand and contract. Suppose for now that when the engine extracts heat from the hot reservoir, it does so *quasistatically*, i.e. slowly enough that the system remains in equilibrium at all times. Use the fundamental thermodynamic relation and the first law of thermodynamics to show $\Delta S_H = -\frac{Q_H}{T_H}$ during one cycle of the engine.

   (c) Similarly, argue that $\Delta S_C = \frac{Q_C}{T_C}$ is the change in entropy of the cold reservoir during one quasistatic cycle of the engine.

   (d) The second law of thermodynamics says that $\Delta S \geq 0$ for any process in a *closed* system. Use this to show $\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H}$.

   (e) Using the definition of the efficiency and your result from part (d), show that $\eta \leq 1 - \frac{T_C}{T_H}$. This is Carnot's theorem. It's sometimes summarized by saying "you can't even break even" in the game of thermodynamics.

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[1] We could be more general and allow for particle flow, but let's keep it simple

(f) Argue that $\Delta S_H$ would be larger if the same amount of heat $Q_H$ were extracted non-quasistatically. Therefore, Carnot's theorem also holds for non-quasistatic engines. In fact, non-quasistatic engines can't achieve the maximum efficiency.

(g) What are some other ways that a heat engine can fail to achieve the maximum efficiency?

**SOLUTION:**

(a) During a full cycle, the engine returns to its original state, so $\oint dU = 0$. Furthermore, we $\oint dQ = Q_H - Q_C$ and $\oint dW = W$. This $W$ is the work done *on* the engine by the surroundings, which by Newton's 3rd law is minus the work done *by* the engine on the surroundings. Putting these contributions together in the first law of thermodynamics, we have

$$W_{\text{by}} = Q_H - Q_C. \tag{1}$$

We recognize this as conservation of energy: the energy expelled in the form of work is equal to the heat taken in minus the heat released. The first law of thermodynamics is an expression of energy conservation.

Now we can compute

$$\eta \equiv \frac{W_{\text{by}}}{Q_H} = 1 - \frac{Q_C}{Q_H}. \tag{2}$$

Since $Q_C$ and $Q_H$ are positive by definition, we have $\eta \leq 1$.

(b) If the hot reservoir remains always in thermal equilibrium (quasistatic process), then $dW_{\text{on H}} = -p_H dV_H$. The first law of thermodynamics, applied to the hot reservoir, then reads

$$dU_H = dQ_{\text{into H}} + dW_{\text{on H}}. \tag{3}$$

Meanwhile, the fundamental thermodynamic relation for the hot reservoir is

$$dU_H = T_H dS_H - p_H dV_H. \tag{4}$$

Combining these, and using the quasistatic relation $dW_{\text{on H}} = -p_H dV_H$, we have

$$dQ_{\text{into H}} = T_H dS_H. \tag{5}$$

Since $\oint dQ_{\text{into H}} = -Q_H$, and $T_H$ doesn't change during the cycle, we have

$$\Delta S_H = -\frac{Q_H}{T_H}. \tag{6}$$

(c) Applying exactly the same argument to the cold reservoir, we find

$$dQ_{\text{into C}} = T_C dS_C. \tag{7}$$

This time $\oint dQ_{\text{into C}} = +Q_C$, so

$$\Delta S_H = \frac{Q_C}{T_C}. \tag{8}$$

(d) During one cycle, the engine returns to its original state, so $\Delta S_{\text{engine}} = 0$. Therefore, applying the 2nd law of thermodynamics to the closed system (hot reservoir + cold reservoir + engine), we find

$$\Delta S = \Delta S_{\text{engine}} + \Delta S_H + \Delta S_C \geq 0 \tag{9}$$

which, upon inserting the results of (b) and (c), gives

$$\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H}. \tag{10}$$

(e) From (a), we have

$$\eta = 1 - \frac{Q_C}{Q_H}. \tag{11}$$

Inserting the inequality from (d), we find

$$\eta \leq 1 - \frac{T_C}{T_H}. \tag{12}$$

This is a stronger limitation on the efficiency than the $\eta \leq 1$ inequality that we found in part (a). It is possible to construct an engine (e.g. with a Carnot cycle) which saturates this bound, i.e.

$$\eta_{\text{Carnot}} = 1 - \frac{T_C}{T_H}. \tag{13}$$

(f)

(g)

2. **Quasistatic adiabatic processes in an ideal gas**:

The goal of this problem is to understand and prove the following statement:

"Consider a non-monatomic ideal gas with $f$ classical quadratic degrees of freedom, translations included. When such a gas undergoes a quasistatic, adiabatic process, the combination $pV^\gamma$ stays constant, where $\gamma = 1 + \frac{2}{f}$."

This is a useful fact to know. For example, a quasistatic adiabatic process occurs in two of the four steps of a Carnot engine. If the working substance of the Carnot engine is an ideal gas, this fact lets us relate the pressure to the volume during the process. Plus, the derivation is interesting!

(a) First, run through the regular proof to understand what goes into it. Using the fundamental law of thermodynamics and the ideal gas law, show that $pV^\gamma$ is a constant for an isentropic (adiabatic) process of an ideal gas. Here, $\gamma = 1 + 2/f$, where $f$ is the number of quadratic degrees of freedom of the gas. Do not assume any particular value of $f$.

(b) Now let's think about what this means. Consider a non-monatomic ideal gas with $N$ particles, volume $V$ and temperature $T$. Show that the partition function for the whole $N$-particle system can be factorized as

$$Z = Z_{\text{monatomic}} Z_{\text{internal}}^N, \tag{14}$$

where $Z_{\text{monatomic}}$ is the partition function of a *monatomic* ideal gas with the same $N$, $V$ and $T$, and

$$Z_{\text{internal}} = \sum_i e^{-\beta \varepsilon_i} \tag{15}$$

where $i$ label the different internal states of motion of a single gas particle, i.e. the different states of rotation and vibration, and $\varepsilon_i$ are the corresponding energies. (In other words, $Z_{\text{internal}}$ would be the partition function of a single gas particle if it weren't allowed to move around the box).

(c) In certain simple cases, the sum in (15) can be evaluated exactly. For example, this was done in Lecture 6 for the vibrational and rotational states of an idealized CO molecule.

For gases with more complicated internal degrees of freedom, we can still say something useful if we assume that the spacing between the internal energy levels $\varepsilon_i$ is small compared to $k_B T$. This can be considered the high-temperature limit, and it happens to be a very good approximation in many cases of practical interest.

Then the energy levels can be treted as a continuum and (15) can be replaced by an integral. We have seen explicit examples of this limit in the lecture notes and homework 3. In general, though, there is a prescription for dealing with systems for which the energy levels can be treated as a continuum–classical mechanics! In the previous discussion, we wrote down the partition function for a system which can be treated with classical mechanics. Adapted to the present context, we have

$$Z_{\text{internal}} = \int \frac{d^D q \, d^D p}{(2\pi\hbar)^D} e^{-\beta H(q,p)}. \tag{16}$$

In this expression, the $q_1, \ldots, q_D$ are the generalized coordinates (from classical mechanics) needed to describe the internal degrees of freedom of the system.

We know that the different quadratic degrees of freedom go into the Hamiltonian, and we can obtain the internal energy of the gas from the partition function. Having done the proof in part (a), do you see how the number of quadratic degrees of freedom shows up in $pV^\gamma$?

**SOLUTION:**

(a) In an isentropic process, $dS = 0$. From the fundamental law of thermodynamics, we have that

$$T dS = dU + p dV, \tag{17}$$

which implies $dU = -p dV$ in the isentropic case. For an ideal gas with fixed $N$ (and with any number $f$ of internal degrees of freedom), the equipartition theorem gives

$$dU = \frac{f}{2} N k_B dT. \tag{18}$$

Therefore,

$$\frac{f}{2} N k_B dT = -p dV. \tag{19}$$

Now we want to write $dT$ in terms of pressure and volume to obtain an expression just in terms of those quantities. Using the ideal has law, which also holds for any $f$, we get

$$dT = \frac{1}{Nk_B}(pdV + Vdp). \tag{20}$$

Then Eq. 19 becomes

$$\frac{f}{2}(pdV + Vdp) = -pdV, \tag{21}$$

$$Vdp = -\left(1 + \frac{2}{f}\right)pdV, \tag{22}$$

$$\frac{1}{p}dp = -\left(1 + \frac{2}{f}\right)\frac{1}{V}dV. \tag{23}$$

We now plug in $\gamma = (1 + \frac{2}{f})$ and integrate both sides to obtain

$$\int_{p_i}^{p_f} \frac{1}{p}dp = -\gamma \int_{V_i}^{V_f} \frac{1}{V}dV, \tag{24}$$

$$\log\left(\frac{p_f}{p_i}\right) = -\gamma \log\left(\frac{V_f}{V_i}\right) = \gamma \log\left(\frac{V_i}{V_f}\right) \tag{25}$$

$$\left(\frac{p_f}{p_i}\right) = \left(\frac{V_i}{V_f}\right)^{\gamma} \tag{26}$$

$$p_f V_f^{\gamma} = p_i V_i^{\gamma}. \tag{27}$$

Therefore, the product $pV^{\gamma}$ is constant for an ideal gas undergoing an isentropic process.

(b) The energy of the $n$th gas particle can be written as

$$\frac{\vec{p}_n^2}{2m} + \varepsilon_{i_n}. \tag{28}$$

Here $\vec{p}_n$ is the center-of-mass momentum of the particle, and $i_n$ is a label that characterizes the various possible internal states of the particles, with associated internal energies $\varepsilon_{i_n}$. Remembering the factor $1/N!$ for indistinguishable particles, we have for the partition function of the whole gas

$$Z = \frac{1}{N!}\left(\sum_{\vec{p}_1}\sum_{i_1}\sum_{\vec{p}_2}\sum_{i_2}\cdots\right) e^{-\beta \sum_n \left(\frac{\vec{p}_n^2}{2m} + \varepsilon_{i_n}\right)} \tag{29}$$

$$= \left[\frac{1}{N!}\left(\sum_{\vec{p}_1}\sum_{\vec{p}_2}\cdots\right) e^{-\beta \sum_n \frac{\vec{p}_n^2}{2m}}\right]\left[\left(\sum_{i_1}\sum_{i_2}\cdots\right) e^{-\beta \sum_n \varepsilon_{i_n}}\right]. \tag{30}$$

The first squared-bracket factor is precisely the sum that occurs in the monatomic ideal gas, i.e. it is equal to $Z_{\text{monatomic}}$. The second squared-bracket factor can be further factorized as $Z_{\text{internal}}^N$, where $Z_{\text{internal}}$ is defined above.

(c)