Problem 1: Doppler broadening of spectral lines

A gas of atoms, each of mass m, is maintained at the absolute temperature T inside an enclosure. The atoms emit light which passes (in the x-direction) through a window of the enclosure and can then be observed as a spectral line in a spectroscope. A stationary atom would emit light at the sharply defined frequency ν_0. But, because of the Doppler effect, the frequency of the light observed from an atom having an x-component of velocity v_x is not simply equal to the frequency ν_0, but is given approximately by

$$\nu = \nu_0(1 + \tfrac{v_x}{c}), \tag{1}$$

where c is the velocity of light. As a result, not all of the light arriving at the spectroscope is at the frequency ν_0; instead it is characterized by some intensity distribution $I(\nu)d\nu$ giving the fraction of light intensity lying in the frequency range between ν and $\nu + d\nu$.

(a) Calculate the mean frequency ν of the light observed in the spectroscope.

(b) Calculate the dispersion $\langle(\Delta\nu)^2\rangle = \langle(\nu - \langle\nu\rangle)^2\rangle$ in the frequency of the light observed in the spectroscope.

(c) Show how measurements of the width $\Delta\nu = \langle(\Delta\nu)^2\rangle^{1/2}$ of a spectral line observed in the light coming from a star allow one to determine the temperature of that star.

Problem 2: Specific heat of an ideal gas

We have derived the Maxwell distribution for an ideal gas in class and in H-W13. Assume the system is a monoatomic molecular gas at the temperature T with N molecules in a box with volume V.

1) Calculate the average kinetic energy $\langle \epsilon \rangle$ where $\epsilon = \frac{1}{2}mv^2$, and the isochoric specific heat C_V.

In fact, if the energy contains a quadratic term, it will contribute to the specific heat $\frac{1}{2}k_B$ per atom. This is called the equipartition theorem, which is only valid for the classic statistical mechanics.

2) Using the result of Eq. 5 to calculate C_V again, and check the consistency. You need to calculate $\langle \epsilon^2 \rangle$ by using the Maxwell distribution.

Problem 3: The partition function and the quantum oscillator

Suppose that a system has many possible configurations, i.e., states, labeled by $i = 1, 2, ...$, whose energy is ϵ_i. The system is at the temperature T. The probability that the system lies in each configuration obey the Boltzmann distribution, i.e., $P_i = Z^{-1} e^{-\beta\epsilon_i}$, where $\beta = 1/(k_B T)$ and

$$Z(\beta) = \sum_i e^{-\beta\epsilon_i}, \tag{2}$$

is called the partition function. (In Mathematics or field theory, Z is called the generation function.) The internal energy U, which is defined as the average value of $\langle\epsilon\rangle$,

$$U(\beta) = Z^{-1} \sum_i \epsilon_i e^{-\beta\epsilon_i}. \tag{3}$$

1) Prove that

$$U(\beta) = -\frac{\partial \ln Z}{\partial \beta}. \tag{4}$$

2) The specific heat $C = \frac{dU}{dT} = -k_B \beta^2 \frac{dU}{d\beta}$, please find its expression in terms of the partition function.

3) Prove that

$$C = \frac{1}{k_B T^2} (\langle\epsilon^2\rangle - (\langle\epsilon\rangle)^2. \tag{5}$$

This means that specific heat measures the fluctuations of energy.

4) Consider a set of N harmonic oscillators with the frequency ω. Quantum mechanics tells us that such a harmonic oscillator can only lie in the states with discrete energies at $(n + \frac{1}{2})\hbar\omega$ with $n = 0, 1, 2, 3, ...$ Calculate the internal energy U of such a system, and its specific heat C_V.

5) Take the limits of $k_B T \ll \hbar\omega$ and $k_B T \gg \hbar\omega$ of C_V you calculated in 4). Compare the results with the equipartition theorem.

Problem 4: The Carnot cycle

In class, we have explained the Carnot cycle. The system starts from a state A denoted by its pressure and volume (P_a, V_a). Then it expands isothermally to the state B marked (P_b, V_b) at temperature T_1. Then it expands adiabatically to the state C with (P_c, V_c). Then it undergoes an isothermal compression to the state D with (P_d, V_d) at temperature T_2. Then it returns to the state A by an adiabatical compression.

1) Show that the work done in this cycle equals the area enclosed by the four segments of curves.

2) Assume that working substance is an ideal gas with $\gamma = C_P/C_v$. Calculate the work done, heat transfer, and the entropy change during each step of $A \to B$, $B \to C$, $C \to D$, and $D \to A$, respectively.

3) Confirm that the efficiency of the heat engine $\eta = 1 - \frac{T_2}{T_1}$.

Problem 5: The thermodynamic temperature and entropy

One formulation of the 2nd law of thermodynamics is that it is impossible to completely convert heat form a single reservoir to work in a cynical process in which the system returns to the initial state. Based on this statement, please prove the following results.

1) Consider two reservoirs 1 and 2 with temperatures T_1 and T_2, respectively. Assume $T_1 > T_2$. Two thermal engines 1 and 2 work between these two reservoirs. Engine 1 is reversible and 2 is irreversible. Prove that the efficiency η_1 of engine 1 is higher than the efficiency η_2 of engine 2, i.e., $\eta_1 > \eta_2$.

2) Consider two reversible thermal engines 1 and 2. Prove that their efficiencies should be equal, i.e., $\eta_1 = \eta_2$. Hence, the efficiency of a reversible thermal engine is only determined by the temperatures of the reservoirs, independent of the concrete working substances.

Below, we denote $Q_1/Q_2 = f(T_1, T_2)$, where Q_1 and Q_2 are the heat transfers with the reservoirs 1 and 2, respectively. Obviously, $f(T_1, T_2)f(T_2, T_1) = 1$.

3) Consider three heat reservoirs at temperatures $T_1 > T_2 > T_3$. Three thermal engines working between reservoirs 1 and 2, between 2 and 3, and between 3 and 1, respectively. Prove that $f(T_1, T_3) = f(T_1, T_2)f(T_2, T_3)$. (Be careful, it is not so obvious as it looks! You need to present reasonings.).

Then prove that $f(T_1, T_2)$ can be factorized as

$$f(T_1, T_2) = \phi(T_1)/\phi(T_2).$$

Explain that why $\phi(T)$ is an ascending function of T. Then we can use this fact as the definition of temperature, i.e, assigning $T = \phi(T)$. This is the definition of the thermodynamic temperature.

4) Consider a reversible thermal engine evolving its state from a to b along two different paths 1 and 2. Prove that the following integral is interdependent from the concrete path, i.e.,

$$\int_{1,a}^{b} \frac{dQ}{T} = \int_{2,a}^{b} \frac{dQ}{T}.$$

According to this, we can define $dS = dQ/T$ as a total derivative independent of paths, such that the entropy S is a state function of matter.