

8.08 Statistical Physics II — Spring 2019

Recitation Note 2

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1 Classical Ideal Gas

We review some basic thermodynamic properties of classical ideal gas.

1.1 Partition Function

Consider a canonical ensemble of N non-interacting atoms in d dimensions. The Hamiltonian with Hamiltonian $H = \sum_{i=1}^N \mathbf{p}_i^2/2m$. We first compute the partition function “naively”. Because of the uncertainty principle $\Delta x_i \Delta p_i = h$, each valid state occupies volume h in the phase space. It follows

$$Z = \int \prod_{i=1}^N \left[\frac{d^d \mathbf{p}_i d^d \mathbf{x}_i}{h^d} \exp \left(-\frac{\beta \mathbf{p}_i^2}{2m} \right) \right] \quad (1)$$

$$= \left[\int \frac{d^d \mathbf{p} d^d \mathbf{x}}{h^d} \exp \left(-\frac{\beta \mathbf{p}^2}{2m} \right) \right]^N \quad (2)$$

$$= \left[\frac{V}{h^d} \int d^d \mathbf{p} \exp \left(-\frac{\beta \mathbf{p}^2}{2m} \right) \right]^N \quad (3)$$

$$= \left(\frac{V}{\lambda_T^d} \right)^N, \quad (4)$$

where the thermal wavelength

$$\lambda_T = \left(\frac{2\pi\beta\hbar^2}{m} \right)^{1/2} = \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{1/2}. \quad (5)$$

Here we have used the fact $\int_{-\infty}^{+\infty} e^{-x^2/A} = \sqrt{A\pi}$ and $\hbar = h/2\pi$.

This seemingly innocuous result is physically incorrect. The free energy,

$$F = -k_B T \ln Z = -k_B T N \ln \left(\frac{V}{\lambda_T^d} \right), \quad (6)$$

is not extensive, i.e. $F \propto N \ln V$ instead of $F \propto N$. Therefore, quantities like the entropy $S = -(\partial F/\partial T)_V$ is not extensive either. This can actually leads to the violation of the second law of thermodynamics by a thought experiment called the “Gibbs paradox”. We leave the detail to curious readers: [Wikipedia page of Gibbs paradox].

The origin of the paradox is that we did not account for the indistinguishability of the atoms. To remedy the problem, we simply multiply a factor of $1/N!$ such that

$$Z = \frac{1}{N!} \left(\frac{V}{\lambda_T^d} \right)^N. \quad (7)$$

The resulting free energy is then

$$F = -k_B T \ln Z = -k_B T \left[-N \ln N + N + N \ln \left(\frac{V}{\lambda_T^d} \right) \right] = k_B T N [\ln(n\lambda_T^d) - 1], \quad (8)$$

where $n \equiv N/V$ is the density and we have used the Stirling approximation $\ln n! \approx x \ln x - x$ (note that here we need to keep the approximation it to the subleading order). This free energy is obviously extensive.

1.2 Thermodynamic Properties

- The internal energy can be computed as

$$U = -\frac{\partial \ln Z}{\partial \beta} = \frac{Nd k_B T}{2}, \quad (9)$$

which is also extensive. It is important to note the internal energy is only a function of the temperature.

This result is called the “equipartition of energy”, i.e. each translation degrees of freedom contributes $k_B T/2$ to the internal energy¹. The heat capacity is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{Ndk_B}{2}. \quad (10)$$

- The entropy can be computed as

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = Nk_B \left[1 + \frac{d}{2} - \ln(n\lambda_T^d) \right], \quad (11)$$

which is also extensive.

For an adiabatic (also called isentropic) process, i.e. $\Delta S = 0$, we have $n\lambda_T^d = \text{const.}$ or $T^{d/2}V = \text{const.}$

- The pressure of the system

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{k_B T N}{V}, \quad (12)$$

which can be rewritten as

$$pV = Nk_B T, \quad (13)$$

or

$$pV = nRT, \quad (14)$$

where $R \equiv N_A k_B$ is the ideal gas constant. The above two equations are the well-known equation of state of classical ideal gas.

In fact, it is possible to derive the adiabatic relation in a general setting. By using

$$dU = -pdV = C_v dT, \quad (15)$$

$$dH = Vdp = C_p dT, \quad (16)$$

we have

$$\frac{dp/p}{dV/V} = -\frac{C_p}{C_v} \equiv -\gamma. \quad (17)$$

Integrate both sides, it follows

$$pV^\gamma = \text{const.} \quad (18)$$

The above result is independent of the ideal gas. Insert the equation of state of the ideal gas to eliminate p , we have $TV^{\gamma-1} = \text{const.}$ For ideal gas, the relation $C_p - C_v = Nk_B$ always holds true (the proof is left as an exercise, whose answer can be found on [this webpage]). It is then straightforward to verify $TV^{\gamma-1} = \text{const.}$ is equivalent to $T^{d/2}V = \text{const.}$

Before concluding this section, we point out although statistical mechanics was developed in the 19th century, it actually hints the existence of quantum mechanics. There are at least two hints hidden in the above results:

1. The Gibbs paradox requires the notion of “indistinguishability”, a notion that is not obvious in classical mechanics because every particle is perfectly measurable and trackable, and therefore distinguishable.
2. It is not obvious why each valid state of the particle occupies volume h in the phase space. Note that since both internal energy and the equation of state do not involve h , and the absolute value of free energy or entropy is not measurable, the exact value of h has no physical consequence. However, each valid state must occupy **some** volume in the phase space and it is not clear what a priori value should be.

¹Note that each degrees of freedom of a harmonic oscillator contributes $k_B T$ at high temperature, as computed in the last recitation. This is different from the translation degrees of freedom.

2 Carnot Cycle

2.1 Ideal Gas in Carnot Engine

Heat engine works between two heat baths of different temperatures. It converts the heat to the mechanical energy by bringing its work substance from high temperature to low temperature. The efficiency of the heat engine is defined by

$$\eta \equiv \frac{-W}{Q_h} = \frac{Q_h + Q_c}{Q_h}, \quad (19)$$

where $W < 0$ is the work extracted from the engine, $Q_h > 0$ is the heated obtained by the engine from the hot bath, and $Q_c < 0$ is the heat given by the engine to the cold bath. The equality holds because of the conservation of energy $Q_h = -W - Q_c$.

In the following we consider a particular type of heat engine. Its work substance is the three-dimensional ideal gas. It operates by performing the so-called ‘‘Carnot cycle’’, and the engine is called the ‘‘Carnot engine’’.

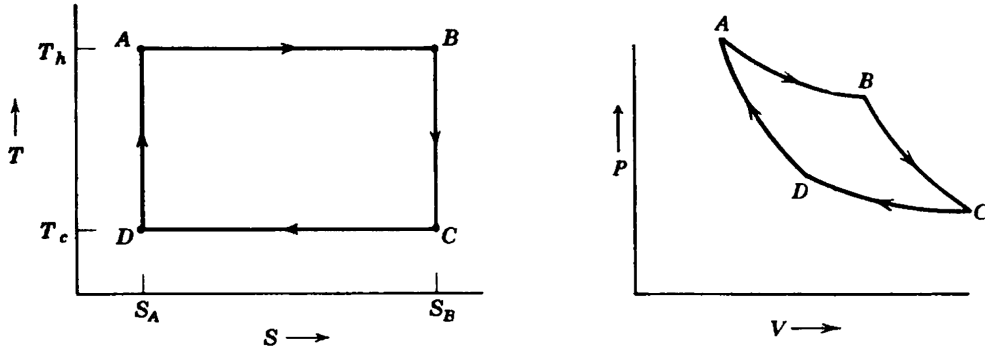


Figure 1: The $T - S$ and $P - V$ diagram of Carnot cycle.

1. AB is an isothermal expansion. According to Eq. (11) and (9),

$$\Delta S_{AB} = Nk_B \ln \left(\frac{V_B}{V_A} \right), \quad \Delta U_{AB} = 0. \quad (20)$$

Since $\Delta U = T\Delta S + W$,

$$Q_{AB} = Nk_B T_h \ln \left(\frac{V_B}{V_A} \right) > 0, \quad W_{AB} = -Nk_B T_h \ln \left(\frac{V_B}{V_A} \right). \quad (21)$$

The work can also be computed from the equation of state,

$$W_{AB} = \int_{V_A}^{V_B} -pdV = \int_{V_A}^{V_B} -\frac{Nk_B T_h}{V} dV = -Nk_B T_h \ln \left(\frac{V_B}{V_A} \right). \quad (22)$$

2. BC is an adiabatic expansion.

$$\Delta S_{BC} = 0, \quad \Delta U_{BC} = \frac{3Nk_B(T_c - T_h)}{2}. \quad (23)$$

It follows

$$Q_{BC} = 0, \quad W_{BC} = \frac{3Nk_B(T_c - T_h)}{2}. \quad (24)$$

3. CD is an isothermal compression.

$$Q_{CD} = Nk_B T_c \ln \left(\frac{V_D}{V_C} \right) < 0, \quad W_{CD} = -Nk_B T_c \ln \left(\frac{V_D}{V_C} \right). \quad (25)$$

4. DA is an adiabatic compression.

$$Q_{DA} = 0, \quad W_{DA} = \frac{3Nk_B(T_h - T_c)}{2}. \quad (26)$$

Use the fact that $T^{3/2}V = \text{const.}$ in an adiabatic process,

$$\frac{V_C}{V_B} = \frac{V_D}{V_A} = \left(\frac{T_h}{T_c} \right)^{3/2}. \quad (27)$$

Combining all above,

$$\eta = -\frac{W_{AB} + W_{BC} + W_{CD} + W_{DA}}{Q_{AB}} = \frac{Q_{AB} + Q_{CD}}{Q_{AB}} = 1 - \frac{T_c}{T_h}. \quad (28)$$

Note that this efficiency is always smaller than one.

2.2 Carnot Engine Efficiency as a Characterization of Temperature

Previously in this course, we have defined temperature from thermal equilibrium, i.e., two systems in thermal equilibrium share the same temperature. This is called the “zeroth law of thermodynamics” and is proved using statistical mechanics (if you don’t know how to prove it, check the lecture note or the last recitation note). The problem with this definition is that it does not provide a practical way to measure the temperature.

On the other hand, we have seen that the efficiency of the Carnot cycle is a function of temperatures alone. Moreover, in fact, the efficiency we just obtained is the best one can have between two heat baths of temperature T_h and T_c . This is the [Carnot’s theorem]:

- All heat engines between two heat baths are less efficient than a Carnot engine operating between the same baths;
- Every Carnot engine between a pair of heat baths is equally efficient, regardless of the working substance employed or the operation details.

With the help of the universality of Carnot’s theorem, temperature can be measured from the efficiency of Carnot engines. This provides a universal way to characterize temperature or even define temperature².

2.3 Reversed Carnot Cycle and Refrigeration

One can turn a Carnot heat engine into a refrigerator by simply reversing the Carnot cycle. The reversed Carnot cycle extracts heat from the cold heat bath to the hot heat bath with the price of additional work. The efficiency of a refrigerator is defined by

$$\eta \equiv \frac{Q_c}{W} = 1 - \frac{Q_h}{W}, \quad (29)$$

where $W > 0$ is the work done to the refrigerator, $Q_c > 0$ is the heat obtained by the refrigerator from the cold bath and $Q_h < 0$ is the heat given by the refrigerator to the hot bath. For a refrigerator that runs a reversed Carnot engine, it is

$$\eta = \frac{Q_{DC}}{W_{AD} + W_{DC} + W_{CB} + W_{BA}} = \frac{Q_{CD}}{W_{DA} + W_{CD} + W_{BC} + W_{AB}} = \frac{T_c}{T_h - T_c}. \quad (30)$$

²However, the correctness of Carnot’s theorem relies on the second law of thermodynamics, which is independent of the zeroth law. Also, so far there is no general way to prove the second law of thermodynamics from statistical mechanics. Therefore it is logically plausible to imagine a world that zeroth law holds but the second law does not. In that case one cannot define temperature from Carnot engine efficiency.

Note that the efficiency can be greater than one, and tends to be zero if T_c goes to zero. This suggests that the system is harder to cool when the system approaches to absolute zero temperature. In fact, the third law of thermodynamics states that absolutely zero temperature can never be reached in a finite number of operations.

2.4 Ultralow Temperatures of Condensed Matter

In the pset, you will compute how temperature changes in adiabatic demagnetization, a process very similar to reversed Carnot cycle where the work substance is the spin paramagnet instead of the ideal gas. Adiabatic demagnetization is actually the state-of-the-art method of reaching ultralow temperature in condensed matter systems (the temperature can be much lower in atomic gas systems).

Table 1: Dominantly used refrigeration techniques in different temperature ranges. Taken from [1].

Method	Typical Temperature	Record Temperature
Liquid Nitrogen	77K	
Helium-4 evaporation	1.3K	0.7K
^3He - ^4He dilution	10mK	2mK
Nuclear magnetic refrigeration	100 μK	1.5 μK

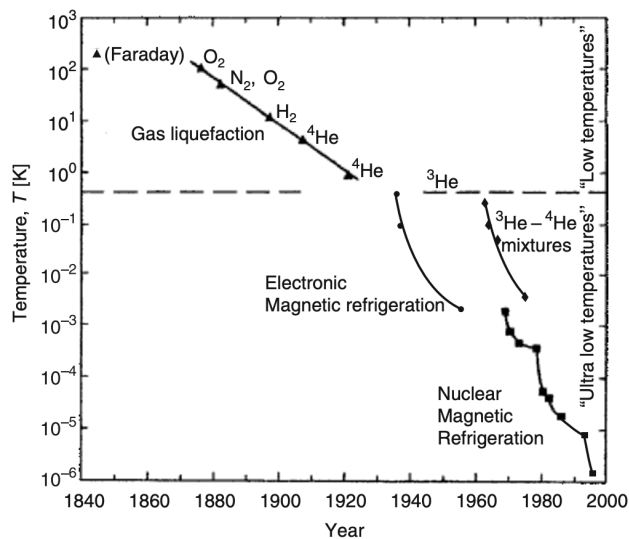


Figure 2: Historical development of refrigeration temperatures of condensed matter. Taken from [1].

References

- [1] Frank Pobell. *Matter and Methods at Low Temperatures*, pages 1–6. Springer Berlin Heidelberg, Berlin, Heidelberg, 2007.