Review of thermodynamics

What is thermodynamics?

- Historic roots: unknown microscopic structure of matter, substance of heat – phlogiston, specific laws of heat phenomena (irreversibility)
- Modern thermodynamics: no reference to microscopic structure of matter, precise mathematical formulation (exact differential, state function, integrating factor), universal character
- Equilibrium systems, static or quasi-static phenomena
- Not only gases but ...

Thermodynamic quantities

- Extensive and intensive quantities
- Pressure p
- Work
  $$dW = pdV \tag{1}$$
  $dW > 0$ or $dW < 0$
- Heat Q
- Temperature T, no reference to $U = \frac{3}{2}Nk_BT$

Equation of state

$$f(p, V, T) = 0 \tag{2}$$

Ideal gas

$$pV = nRT \tag{3}$$

n – number of mols, $R \approx 8.3\ \frac{\mathrm{J}}{\mathrm{mol \cdot K}}$ – gas constant

$$nR = Nk_B \tag{4}$$

$k_B = 1.38 \cdot 10^{-23}\ \frac{\mathrm{J}}{\mathrm{K}}$ – Boltzmann constant, N – number of atoms or molecules

$$pV = Nk_BT \tag{5}$$

0-th principle of thermodynamics

- Thermal contact
- Thermal equilibrium of systems A & $B \Longrightarrow$ no heat transfer

- 0-th principle of thermodynamics: A & B in thermal equilibrium and B & C in thermal equilibrium $\Longrightarrow$ A & C in thermal equilibrium (transitive character of thermal equilibrium)

Thermodynamical processes

- Quasi-stationary processes
- Isochoric processes $V = \text{const}$
- Isothermal processes $T = \text{const}$
- Isobaric processes $p = \text{const}$
- Adiabatic processes $dQ = 0$
- Reversible and irreversible processes

Exact differential

- Exact differential of the function $f(x_1, x_2, \ldots, x_n)$

$$df = X_1 dx_1 + X_2 dx_2 + \ldots X_n dx_n \tag{6}$$

$$\frac{dX_i}{dx_j} = \frac{dX_j}{dx_i}, \qquad i, j = 1, 2, \ldots, n \tag{7}$$

If the function is explicitly known

$$df = \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 + \cdots + \frac{\partial f}{\partial x_n} dx_n \tag{8}$$

$$\frac{\partial^2 f}{\partial x_i \partial x_j} = \frac{\partial^2 f}{\partial x_j \partial x_i} \tag{9}$$

- Path independence of the integral

$$\int_A^B df = f(B) - f(A) \tag{10}$$

A & B initial and final sets of the variables $(x_1, x_2, \ldots, x_n)$.

State function

- The state function fully depends on a state of a system but not on a process by which state is reached.
- If F is the state function, dF is exact differential.

1-st principle of thermodynamics

- Energy of the system U is the state function and

$$dU = dQ - dW \tag{11}$$

- dU is the exact differential but dQ and dW are not. Q and W are not state functions.
- Heat can be converted into work!

2-nd principle of thermodynamics

- $dS = \frac{dQ}{T}$, where dQ is the heat transfer in reversible process, is the exact differential.
- S – entropy is the state function
- $$\int_A^B \frac{dQ}{T} \le S(B) - S(A) \tag{12}$$
  The equality is for a reversible and inequality for irreversible process.
- $dQ = 0 \Longrightarrow S(A) \le S(B)$ – 'entropy of an isolated system is a non-decreasing function of time'

Temperature as integrating factor

- If $df = X_1 dx_1 + X_2 dx_2 + \cdots + X_n dx_n$ is not exact differential but hdf is, h is the integrating factor of df.
- In thermodynamics T is the integrating factor of dQ.
- How does it work for an ideal gas?

  Express dQ through (V,T), (V,p) or (T,p) using $dU = dQ - pdV$, $pV = nRT$ and $U = C_V T$. Show that dQ/T is the exact differential for every set of variables.

Independence of ideal-gas energy of gas volume

- Trivial problem in statistical mechanics. Since $U = \frac{3}{2} N k_B T$, then
  $$\left(\frac{\partial U}{\partial V}\right)_T = 0. \tag{13}$$
- How to prove it in thermodynamics?
- Using the first and the second principle of thermodynamics one finds
  $$dS = \frac{dQ}{T} = \frac{dU + pdV}{T} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV. \tag{14}$$
- Since dS is exact differential we have
  $$\left(\frac{\partial}{\partial V}\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\right)_V. \tag{15}$$
- Using the property
  $$\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V, \tag{16}$$
  one finds
  $$\left(\frac{\partial p}{\partial T}\right)_V - \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] = 0, \tag{17}$$
  which gives the equality (13) due to the ideal-gas equation of state
  $$pV = nRT. \tag{18}$$

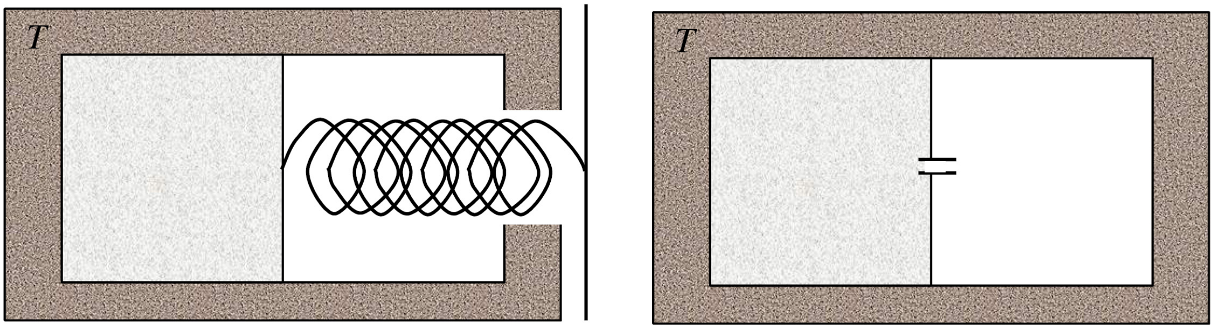

Figure 1: Reversible and irreversible gas decompression

Entropy change in isothermal decompression of ideal gas

We consider the reversible and irreversible isothermal decompression of ideal gas, see Fig. 1. The initial and finals states are the same in both cases: $(T, V_1) \to (T, V_2)$.

- In the reversible process we have

$$\Delta S_{\text{gas}} = \int \frac{dQ}{T} = \frac{Q}{T}. \tag{19}$$

  Since $U =$ const, one finds

$$Q = W = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \frac{V_2}{V_1}, \tag{20}$$

  and

$$\Delta S_{\text{gas}} = nR \ln \frac{V_2}{V_1}. \tag{21}$$

- The entropy change in the irreversible process is the same, because S is the state function.
- Where is the difference? The difference is in the environment: the thermostat and the spring if present.
- $\Delta S = \Delta S_{\text{gas}} + \Delta S_{\text{environment}}$
- In the irreversible decompression $\Delta S_{\text{environment}} = 0$ and $\Delta S = \Delta S_{\text{gas}} > 0$.
- In the reversible decompression $\Delta S_{\text{environment}} = -\Delta S_{\text{gas}}$ and $\Delta S = 0$.

Heat capacity

- Heat capacity is an amount of heat needed to change the temperature by one degree. It depends on external conditions.
- Heat capacity at fixed volume

$$C_V \equiv \left(\frac{\partial Q}{\partial T}\right)_V \tag{22}$$

- Heat capacity at fixed pressure

$$C_p \equiv \left(\frac{\partial Q}{\partial T}\right)_p \tag{23}$$

- The first principle of thermodynamics $dQ = dU + pdV$ provides the relation

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV, \tag{24}$$

when (V, T) are independent variables and

$$dQ = \left[\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\right] dT + \left[\left(\frac{\partial U}{\partial p}\right)_T + p\left(\frac{\partial V}{\partial p}\right)_T\right] dp, \tag{25}$$

when (p, T) are independent variables.

- Consequently

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \tag{26}$$

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p, \tag{27}$$

where $H \equiv U + pV$ is called the enthalpy.

- Specific heat is the heat capacity per unit amount of a given substance. It characterizes a substance not a system.

Mayer equation

- Because of (13) the heat capacity C_V is simplified to

$$C_V = \frac{dU}{dT}, \tag{28}$$

and

$$U = C_V T, \tag{29}$$

if

$$\frac{dC_V}{dT} = 0 \qquad \& \qquad U(T = 0) = 0. \tag{30}$$

- From statistical mechanics we know that the energy of ideal gas is $U = \frac{3}{2} N k_B T$ and the heat capacity, which equals

$$C_V = \frac{3}{2} N k_B, \tag{31}$$

is temperature independent.

- Using Eq. (29) and the ideal-gas equation of state (18), the enthalpy equals

$$H \equiv U + pV = (C_V + nR)T, \tag{32}$$

which gives the Mayer equation

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = C_V + nR, \tag{33}$$

usually written as

$$C_p - C_V = nR > 0. \tag{34}$$

- C_p is bigger than C_V. What is the physical reason?

Adiabatic compression of ideal gas

- When a process is adiabatic ($dQ = 0$), the first principle of thermodynamics reads

$$dU + pdV = 0. \tag{35}$$

- Using Eq. (29) and the ideal-gas equation of state (18), one rewrites the relation (35) as

$$\frac{dT}{T} = -\gamma \frac{dV}{V}, \tag{36}$$

where $\gamma \equiv \frac{nR}{C_V}$. Integrating Eq. (36), we find

$$\ln T = -\gamma \ln V + \text{const.}, \tag{37}$$

where "const." is an arbitrary constant. Eq. (37) can be rewritten as

$$TV^{\gamma} = \text{const.} \tag{38}$$

or using the ideal-gas equation of state (18) as

$$pV^{1+\gamma} = \text{const.} \tag{39}$$

"const." denotes each time a different constant in Eqs. (37, 38, 39).

- Eq. (39) shows that the pressure grows faster in adiabatic than in isothermal compression.

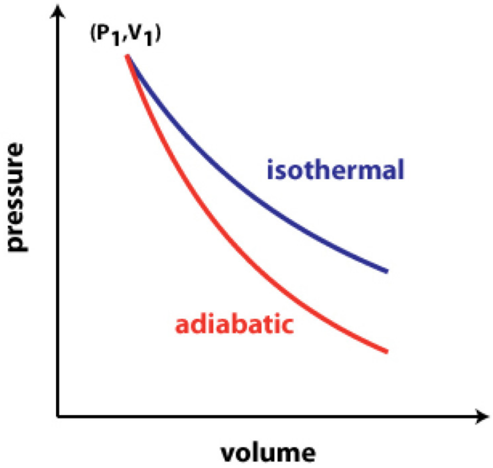

Figure 2: Izothermal vs. adiabatic compression

3-rd principle of thermodynamics

The 2-nd principle of thermodynamics determines the entropy difference in two states of a system of interest. The 3-rd principle allows one to determine an absolute value of the entropy.

- According to the third principle of thermodynamics, the entropy of any system in the temperature of absolute zero is a universal constant which can be chosen as zero.

- It follows from the 3-rd principle that C_p, C_V or any other heat capacity denoted as C vanishes as $T \to 0$.
- Writing dQ as $dQ = C(T)dT$, we have

$$S(T) = \int_0^T \frac{C(T')}{T'}\, dT'. \tag{40}$$

As $T \to 0$ the interval of integration tends to zero. So we use the approximation

$$C(T) = aT^\alpha, \tag{41}$$

where the constant a is independent of T. Substituting (41) into Eq. (40) and performing the integration one gets

$$S(T) = \frac{a}{\alpha}\, T^\alpha. \tag{42}$$

Since $S(T) \to 0$ as $T \to 0$, the power $\alpha > 0$. Consequently, $C(T) \to 0$ as $T \to 0$.

- The result is in conflict with the formula (31) which is obtained in classical statistical mechanics. At low temperature quantum effects have to be taken into account.
- Vanishing of C as $T \to 0$ shows that $T = 0$ is unreachable.

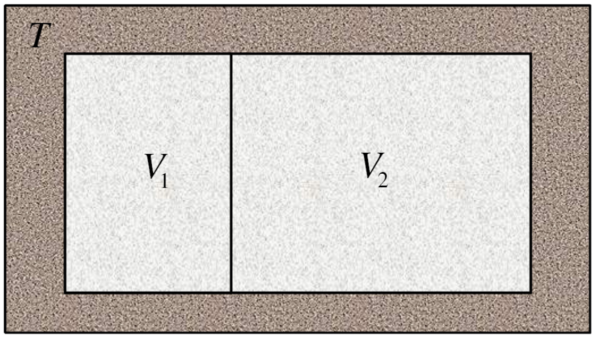

Figure 3: How to get a position of the movable divider?

Free energy

- Free energy F is defined as $F \equiv U - TS$.
- What for it is? A minimum of F determines a system's state at fixed T and V.
- Using the first and second principle of thermodynamics (for reversible processes), one writes

$$dF = dU - SdT - TdS = -pdV - SdT, \tag{43}$$

As seen $dF = 0$ if $dV = 0$ and $dT = 0$. So, there is extremum of F if T and V are fixed.

- Since in general $dQ \le TdS$, we get

$$dF = dQ - TdS \le 0. \tag{44}$$

for $dV = dT = 0$. So, there is minimum of F if T and V are fixed.

- As a simple application of F consider a system depicted in Fig. 3. Where is an equilibrium position of the movable divider?
- $V = V_1 + V_2$, $T_1 = T_2 = T$ and $F = F_1(V_1) + F_2(V - V_1)$. The condition of a minimum is

$$\left(\frac{\partial F}{\partial V_1}\right)_T = \left(\frac{\partial F_1}{\partial V_1}\right)_T + \left(\frac{\partial F_2}{\partial V_1}\right)_T = \left(\frac{\partial F_1}{\partial V_1}\right)_T - \left(\frac{\partial F_2}{\partial V_2}\right)_T = 0, \tag{45}$$

which gives

$$\left(\frac{\partial F_1}{\partial V_1}\right)_T = \left(\frac{\partial F_2}{\partial V_2}\right)_T. \tag{46}$$

- What does it mean? Since $dF = -pdV - SdT$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T. \tag{47}$$

Therefore, the condition (45) means

$$p_1 = p_2. \tag{48}$$

Free enthalpy

Going from (V, T) to (p, T), we need another function different than F to determine a system's state.

- Free enthalpy G is defined $G = F + pV$.
- When T and p are fixed, a minimum G determines a system's state.