Important formulas (learn these by heart!)

Note: if the temperature T is measured in Kelvins, but not in the energy units, then $T \to k_B T$ in all of the equations below; all quantities containing the change of anything per temperature (e.g., heat capacitance) should also be multiplied by k_B then; you should always be able to recover the Boltzmann constant from dimensions.

Gibbs Distribution

The Gibbs distribution

$$w_i = \frac{e^{-\frac{E_i}{T}}}{Z}, \tag{1}$$

the probability that a generic quantum system is in the i-th state.

The grand-canonical (Gibbs) distribution (when the number of particles N is variable)

$$w_{iN} = \frac{e^{\mu N - \frac{E_{iN}}{T}}}{Z}, \tag{2}$$

where iN is the i-th quantum state of a system of N particles.

Classical ideal gas

The Maxwell distribution (follows from the Gibb's distribution)

The probability that the absolute value of a molecule's velocity in an ideal gas (3D) lies in the interval $(v, v + dv)$ is given by $f(v)dv$, with

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi T}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2T}}. \tag{3}$$

The probability that a molecule's velocity in an ideal gas (in 3D) lies in the element $d\mathbf{v}$ near the vector $\mathbf{v}$ is given by $f(\mathbf{v})d\mathbf{v}$, with

$$f(\mathbf{v}) = \left(\frac{m}{2\pi T}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2T}}. \tag{4}$$

Important: do not confuse Eqs. (3) and (4)!!!

Boltzmann distribution

If an ideal gas at temperature T is exposed to an external inhomogeneous potential $U(\mathbf{r})$, then it's concentration depends on the coordinate $\mathbf{r}$ as

$$n(\mathbf{r}) = n_0 \exp\left(-\frac{U(\mathbf{r})}{T}\right).$$

Both the Maxwell and the Boltzmann distributions follow from the Gibbs distribution.

Equation of state:

$$PV = NT$$

(in all dimensions!)

Heat capacity

1. Monoatomic gas: $C_V = \frac{3}{2}N$
2. Diatomic gas: $C_V = \frac{5}{2}N$
3. Each molecule consists of three atoms or more: $C_V = 3N$

Heat capacity (of an ideal has) at constant pressure: $C_P = C_V + N$

Van der Waals equation

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NT, \tag{5}$$

a and b are constants.

First law of thermodynamics = energy conservation law

In a quasistatic process

$$TdS = dE + PdV.$$

(*Hint:* in exam problems all processes are usually quasistatic;))

Here TdS is the amount of heat received by the system (quasistatic process), dE is the change of the internal energy, PdV is the amount of work.

Thermodynamic potentials

$$F = E - TS \tag{6}$$
$$\Phi = E - TS + PV \tag{7}$$
$$H = E + PV \tag{8}$$

Using the differentials of these functions and the first law of thermodynamics, you should be able to obtain the macroscopic parameters in the form of derivatives $S = -\left(\frac{\partial F}{\partial T}\right)_V$, $P = -\left(\frac{\partial F}{\partial V}\right)_T$, $S = -\left(\frac{\partial \Phi}{\partial T}\right)_P$, $V = \left(\frac{\partial \Phi}{\partial P}\right)_T$, $T = \left(\frac{\partial H}{\partial S}\right)_P$, $V = \left(\frac{\partial H}{\partial P}\right)_S$. There is no need to remember these; they follow from Eqs. (6)-(8) in one line.

Then, using these derivatives and the equalities like $\frac{\partial^2 F}{\partial T \partial V} \equiv \frac{\partial^2 F}{\partial V \partial T}$, we obtain the Maxwell's relations

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \tag{9}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T, \tag{10}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P. \tag{11}$$

You do not have to remember those so long as you can derive them in two steps as described above.

A useful relationship between mutual derivatives of three quantities

If one quantity Z is a function of two other quantities X and Y, $Z = Z(X, Y)$, then their derivatives with respect to each other are related as

$$\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \left(\frac{\partial Z}{\partial X}\right)_Y = -1. \tag{12}$$

This relationship is very useful in many thermodynamic problems. For example, you may use it to compute derivates like $\left(\frac{\partial V}{\partial T}\right)_P$ when the equation of state is known in the form $P = P(V, T)$, but V cannot be easily expressed as a function of P and T.

Important relation between microscopic and macroscopic degrees of freedom

When you know the eigenenergies E_i of a quantum system, you may compute its partition function as $Z = \sum_i e^{-\frac{E_i}{T}}$ and immediately obtain the free energy as

$$F = -T \ln Z. \tag{13}$$

If you consider the free energy F as a function of volume V and temperature T, the equation of state may be found immediately as $P = -\left(\frac{\partial F}{\partial V}\right)_T$ (indeed, it's an equation relating the pressure P, volume V and temperature T). The entropy S is given by $S = -\left(\frac{\partial F}{\partial T}\right)_V$ and may be used to compute, e.g., the heat received by the system.

Black-body radiation

<u>Stefan-Boltzmann law</u>

$$j = \sigma T^4 \tag{14}$$

– the power of the radiation emitted by a unit area of the surface of a black body; σ is what is called the Stefan-Boltzmann constant (one is extremely unlikely to be expected to remember its value).

    <u>Planck's law</u>

$$dE_\omega = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\frac{\hbar\omega}{T}} - 1} d\omega \tag{15}$$

– the energy of the radiation components of the black-body radiation with frequencies between ω and $\omega + d\omega$; V is the volume. You do not need need to remember this formula if you can derive it in a couple of minutes. If you can't derive it that quickly, practice until you can.

Bosonic and fermionic systems

$$f(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{T}\right) + 1} \tag{16}$$

– Fermi-Dirac distribution function

$$n_B(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{T}\right) - 1} \tag{17}$$

– Bose-Einstein distribution function

    When the number of bosons is not conserved (phonons, photons, any quantum excitations), $\mu = 0$.

Super important

The number of states of a particle in a d-dimensional system in an element $d\mathbf{k}$ of momentum space (assumed to be significantly larger than the scale of spatial quantisation of momentum)

$$g\frac{V d\mathbf{k}}{(2\pi\hbar)^d}, \tag{18}$$

where g accounts for the degeneracy due to discrete degree of freedom such as spin, valley and polarisation. Use it when computing thermodynamic functions, e.g. energy, for systems of (classical or quantum) ideal gases. For example, you may use it to derive Eq. (15) for an ideal gas of photons.