

Important formulas (learn these by heart!)

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

Gibbs Distribution

Gibbs distribution

$$w_i = \frac{e^{-\frac{E_i}{T}}}{Z}, \quad (1)$$

the probability that a generic quantum system is in the i -th state, where the normalisation constant

$$Z = \sum_i e^{-\frac{E_i}{T}} \quad (2)$$

is called the partition function of the system.

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

$$w_{iN} = \frac{e^{\mu N - \frac{E_{iN}}{T}}}{Z}, \quad (3)$$

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

Classical ideal gas

The Maxwell distribution

In principle, the Maxwell distribution does not need to be remembered, as it follows from Gibbs distribution. It may take a little while to derive. It is recommended that you derive it at least once on your own. If you can do it and understand all the steps, you are good.

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

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

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

$$f(\mathbf{v}) = \left(\frac{m}{2\pi T}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2T}}. \quad (5)$$

Important: do not confuse Eqs. (4) and (5)!!! Eq. (5) is the probability density of the velocity vector \mathbf{v} , while Eq. (4) is the probability density of the absolute value v of this velocity.

Boltzmann distribution

If an ideal gas at temperature T is exposed to an external inhomogeneous potential $U(\mathbf{r})$, then its 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 Gibbs distribution.

Equation of state:

$$PV = NT$$

(in all dimensions!)

Heat capacity (3D)

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 gas) at constant pressure: $C_P = C_V + N$

These equations presume that the gas is classical and the molecules have no vibrational degrees of freedom (which for realistic molecules is justified by the fact that the quantum of vibrations is larger than room temperature) and the moment of inertia of one atom is zero (which means that, e.g., the quantum of rotation of a diatomic molecule about its symmetry axis is infinite and, thus, this rotational degree of freedom is not excited).

Van der Waals equation

Van der Waals gas is a non-ideal gas, often used as a model for describing liquid-gas phase transition. Its equation of state is given by

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NT, \quad (6)$$

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;)), where dS , dE and dV are, respectively, infinitesimal changes of entropy, internal energy and volume.

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.

It is extremely important to remember that in a quasistatic process the quantity

$$\delta Q = TdS$$

gives the amount of heat received by the system. This may be used in a lot of contexts, for example, if you compute the heat capacity for a given process, defined as $C_{process} = \left(\frac{\delta Q}{dT}\right)_{process}$. For example, for a process where the volume of a system is being kept constant, $V = const$, this gives $C_V = T \left(\frac{\partial S}{\partial T}\right)_V$.

Thermodynamic potentials

$$F = E - TS \tag{7}$$

$$\Phi = E - TS + PV \tag{8}$$

$$H = E + PV \tag{9}$$

These are, respectively, the free energy (sometimes referred to as Helmholtz free energy), the thermodynamic potential (sometimes referred to as Gibbs free energy) and enthalpy.

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. (7)-(9) 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

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \quad (10)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T, \quad (11)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P. \quad (12)$$

Note: you do not need to remember those! They can be derived from the definitions of the thermodynamic potentials defined above in two steps. If you are having difficulties deriving them, practise until you can do it quickly.

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

$$\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \left(\frac{\partial Z}{\partial X}\right)_Y = -1. \quad (13)$$

This relationship is very useful in many thermodynamic problems. For example, you may use it to compute derivatives 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

If 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

$$F = -T \ln Z. \quad (14)$$

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.

That usually gives you a way to find the equation of state of any system whose eigenvalues you know.

Black-body radiation

Stefan-Boltzmann law

$$j = \sigma T^4 \quad (15)$$

is 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).

Planck's law

$$dE_\omega = \frac{V \hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\frac{\hbar \omega}{T}} - 1} d\omega \quad (16)$$

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

Bosonic and fermionic systems

$$f(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{T}\right) + 1} \quad (17)$$

= Fermi-Dirac distribution function

$$n_B(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \mu}{T}\right) - 1} \quad (18)$$

= Bose-Einstein distribution function

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

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)

$$g \frac{V d\mathbf{k}}{(2\pi\hbar)^d}, \quad (19)$$

where g accounts for the degeneracy due to discrete degree of freedom such as spin, valley and polarisation, and V is the volume of the system. 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. (16) for an ideal gas of photons.

Example. This formula is also used often when deriving the density of states. Consider, for example, a 3D gas. The momentum volume for the states with momenta between k and $k + dk$ is $4\pi k^2 dk$. If those momenta correspond to the energies of particles between E and $E + dE$, then

$$\nu(E)dE = g \frac{4\pi k^2 dk}{(2\pi\hbar)^3}, \quad (20)$$

where $\nu(E)$ is the density of states and both sides of the equation give the number of states in the energy interval dE . Taking into account that $v = \frac{dE(k)}{dk}$ is the velocity of a particle,

$$\nu(E) = \frac{gk^2}{2\pi^2\hbar^3 v}. \quad (21)$$

Here, one has to express the momentum k and the velocity v as functions of the energy E . For the quadratic dispersion $E(\mathbf{k}) = \frac{k^2}{2m}$, $k(E) = \sqrt{2mE}$ and $v(E) = \sqrt{2E/m}$, leading to

$$\nu(E) = \frac{gVm^{\frac{3}{2}}}{2^{\frac{1}{2}}\pi^2\hbar^3} \sqrt{E}. \quad (22)$$