Making Sense of the Equation Sheet

Physics 213

Fundamental Laws/Principles:

First Law: $dU = dQ + dW$

Energy is conserved—the change in the internal energy of a system is equal to the heat that flows into or out of the system plus the work done on or by the system.

Second Law: $d\sigma/dt \geq 0$

As a system comes to equilibrium, the entropy of the system plus the environment always increases. In equilibrium, the total equilibrium is maximized and does not change in time.

Dimensionless entropy: $\sigma(A) = ln\ \Omega(A), \ \ \Omega(A) = e^{\sigma(A)}, \ \ P(A) \propto \Omega(A)$

$\Omega(A)$ = number of microstates corresponding to the macrostate A, P = probability of observing the macrostate A.

Classical equipartition: Every quadratic degree of freedom has an on average $\frac{1}{2}\ kT$ of thermal energy. This is true provided the characteristic thermal energy scale $kT \gg$ energy level spacing (e.g. $kT \gg \epsilon$, where ϵ is the harmonic oscillator level spacing.) Translational motion persists to zero temperature, therefore equipartition applies at all temperatures.

Entropy and Temperature:

Entropy with dimensions of J/K: $S = k\sigma = k\ ln\Omega$

General definition of temperature: $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$

Anytime two systems exchange energy (keeping the volume and the number of each system constant) their temperatures become equal.

α-Ideal Gases: α = ½ x (number of [quadratic] degrees of freedom) (d.o.f.)

Examples:

Monatomic gas: 3 translational d.o.f. (α = 3/2)

Diatomic gas: 3 translational d.o.f. + 2 rotational d.o.f. (α = 5/2)

Solid ("Einstein"): ~3N oscillators → 3 translational d.o.f. + 3 vibrational d.o.f. (α = 3)

Work done by a gas in an isothermal expansion (T = constant): $W_{by} = NkT \ln(V_f/V_i)$

Relations for an adiabatic process (Q = 0):

$VT^{\alpha} = const.$ $PV^{\gamma} = const.$ $\gamma = (\alpha+1)/\alpha$

Work done in an adiabatic process: $W_{by} = \Delta U = \alpha Nk (T_1 - T_2) = \alpha(P_1V_1 - P_2V_2)$

General expression for the change in entropy when both volume and temperature vary:

$$\Delta S = C_V \ln(T_f/T_i) + Nk \ln(V_f/V_i)$$

Spins:

Binomial distribution: Applies to probabilistic events with two possible outcomes. Examples include coin toss (heads or tails), spins (spin up or spin down), 1-D random walk (step left or step right). If each outcome is equally probable, then the number of microstates corresponding to a particular macrostate is given by

$$\Omega(N, N_{up}) = \frac{N!}{N_{up}!\,(N - N_{up})!}$$

Where N is the number of coin tosses and the macrostate is specified by N_{up}. When N is large, the binomial distribution is approximately given by the Gaussian distribution

$$\Omega(m) = 2^N \sqrt{\frac{2}{\pi N}}\, e^{-m^2/2N}$$

Here, $m = N_{up} - N_{down}$. For a 1-D random walk m is the displacement away from zero. The probability of obtaining a particular macrostate m is $P(m) = \Omega(m)/\Omega_{tot}$, where $\Omega_{tot} = 2^N$ is the total number of microstates.

Spins in a magnetic field: In a magnetic field the magnetic energy of a spin with magnetic moment $\vec{\mu}$ is $E = -\vec{\mu} \cdot \vec{B}$. The net magnetic moment for N spins is

$$\langle M \rangle = N\mu(P_\uparrow - P_\downarrow)$$

To calculate probabilities from the Boltzmann distribution, use

$$P(E) = \frac{d_n\, e^{-E/kT}}{Z}$$

where Z is the partition function.

Z: Sum over all states of the Boltzmann factor $e^{-E_n/kT}$

$$Z = \sum_n d_n \, e^{-E_n/kT}$$

d_n = degeneracy

For a spin in a magnetic field B: $Z = e^{-\mu B/kT} + e^{\mu B/kT}$

Probability for the spin to be aligned parallel to the magnetic field: $P_\uparrow = \dfrac{e^{\mu B/kT}}{Z}$

Probability that the spin and field are aligned antiparallel: $P_\downarrow = \dfrac{e^{-\mu B/kT}}{Z}$

$$\langle M \rangle = N\mu \tanh\left(\frac{\mu B}{kT}\right)$$

High-temperature limit: $\langle M \rangle = N\mu^2 B/kT$. This relationship is known as the Curie Law.

Simple Harmonic Oscillator (SHO):

The quantum harmonic oscillator has equally spaced energy levels $U = n\epsilon$, where $n = 0,1,2,\ldots$ and the energy level spacing is $\epsilon = hf$; h = Planck's constant, and $f = \sqrt{K/m}$ is the classical oscillation frequency.

The probability of the oscillator being in the nth vibrational level is

$$P_n = \frac{e^{-n\epsilon/kT}}{Z},$$

where $Z = \sum_{n=0}^{\infty} e^{-n\epsilon/kT}$. This sum converges to $Z = 1/\left(1 - e^{-\epsilon/kT}\right)$, giving the following result:

$$P_n = \left(1 - e^{-\epsilon/kT}\right)e^{-n\epsilon/kT}.$$

The average energy is

$$\langle E \rangle = \sum_{n=0}^{\infty} n\,\epsilon\, P_n = \frac{\epsilon}{\left(e^{\epsilon/kT} - 1\right)}.$$

When calculating the entropy associated with having q quanta of energy shared among N oscillators, we need to find the number of microstates. The corresponding number of microstates is given by

$$\Omega = \frac{(q + N - 1)!}{q!\,(N - 1)!}$$

Counting:

For $N \gg 1$ use Sterling's approximation, $\ln N! \approx N \ln N - N$

Equilibrium:

When we considered two systems that could exchange volume or energy, we found the equilibrium properties (pressure, density, temperature) by maximizing the combined entropy of both systems. When we consider a small system connected to a large reservoir whose temperature is fixed, then it is more convenient to consider the free energy. This is because the free energy deals only with the entropy and internal energy of the small system. In equilibrium, the free energy of the system must be a minimum. In contrast, the total entropy of the system plus the environment is a maximum.

$$\text{Helmholtz free energy} \equiv F = U_{sys} - T_{env}\, S_{sys}$$

The free energy per particle is the chemical potential: $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$

Ideal gas chemical potential:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -|\Delta| + kT \ln\left(\frac{n}{n_Q}\right)$$

where Δ is the internal energy per particle (in writing $-|\Delta|$ we assume this is a binding energy; for other situations, e.g., gravitational potential energy, it could be positive), $n = N/V$ is the density and $n_Q \approx 1/\Delta V$ is the quantum density. We can loosely think of ΔV as the minimum volume occupied by a single particle. (More precisely, n_Q is the quantum mechanically-constrained maximum number of states per volume that a particle can be in.) From quantum mechanics, we know that particles are not point-like objects. Instead, they have a physical size of order $\lambda(T)$, referred to as the de Broglie wavelength. $\lambda(T)$ depends on temperature. From dimensional arguments, $\Delta V \propto \lambda^3(T)$, thus $n_Q \propto 1/\lambda^3(T)$. The correct quantum mechanical result is $n_Q = \left(\frac{2\pi mkT}{h^2}\right)^{3/2}$.

Putting in the mass of a proton and T = 300K gives $n_Q = 10^{30}$ m^{-3}.

Therefore, we can quickly calculate n_Q for any [monatomic] particle of mass m, at temperature T, using

$$n_Q = (10^{30}\text{m}^{-3})\left(\frac{m}{m_p}\right)^{3/2}\left(\frac{T}{300K}\right)^{3/2}.$$

We can also calculate the 'quantum pressure' (the pressure one would need to compress a gas so that it reached the quantum density, as $p_Q = kT\, n_Q$.

In all the cases we consider, $n \ll n_Q$, therefore the natural log term in μ is negative. Important: this form of the quantum density applies to single-component species (e.g. electrons, protons, and monatomic atoms). If the species has internal degrees of freedom, such as diatomic molecules with rotational and vibrational modes, this simple form of n_Q does not apply, because there are more possible states. Nevertheless, we know that μ will always be lowered by these extra possible states, otherwise the rotations and vibrations simply wouldn't occur.

Chemical potential and equilibrium:

In a reaction involving the creation of different types of particles (examples: interstitial-vacancy pairs and electron-hole pairs in semiconductors), the equilibrium condition is given by

$$\sum_i (\Delta N)_i \, \mu_i = 0$$

where ΔN_i refers to the number of particles of type i involved in the reaction. As an example, consider the chemical reaction
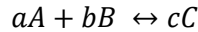
$$aA + bB \leftrightarrow cC$$

where A, B and C refer to the particle type, and a, b, and c are the number of each type. From the general form of the equilibrium condition

$$a\mu_A + b\mu_B = c\mu_C$$

If we treat each species as an ideal gas, liquid, or solid, then

$$\frac{n_C^c}{n_A^a \, n_B^b} = \frac{n_{QC}^c}{n_{QA}^a \, n_{QB}^b} \, e^{\Delta/kT}$$

where $\Delta = c\Delta_c - a\Delta_a - b\Delta_b$.

For the case of a semi-conductor, electrons and holes are created at the same time:

$\mu_e + \mu_h = 0$, so that: $n_e \, n_h = n_{Qe} \, n_{Qh} \, e^{-\Delta/kT} \equiv n_Q^2 \, e^{-\Delta/kT} \equiv n_i^2$.

Here n_i is the "intrinsic" density of electrons (and holes) at a particular temperature. We can also dope the material by substituting in atoms that either give extra free electrons ('donors'), or give extra holes (electron 'acceptors'). The total density will then be, e.g., $n_e = n_i + n_D$.

Phase transitions:

If work is done while reaching equilibrium, then it is the Gibbs free energy which is minimized.

$$\text{Gibbs free energy} = G = U - TS + PV = F + PV$$

In phase transitions, the volume between the two different phases is often different, for example consider a molecule of water going between the liquid and gas phase. We can express the Gibbs free energy involving different phases as

$$G = N_s \, \mu_s + N_l \, \mu_l + N_g \, \mu_g$$

where the subscripts (s, l, g) refer to solid, liquid, and gas, respectively. In equilibrium, the phase with the lowest chemical potential is the stable phase. By maximizing the number of particles corresponding to the phase with the lowest μ, G is minimized.

Thermal Radiation

Thermal-radiation power per unit area radiated by a black body (units W/m^2): $J = \epsilon\, \sigma_{SB}\, T^4$

σ_{SB} = Stefan-Boltzmann constant

ϵ = emissivity. The emissivity of an object must equal its absorptivity. Hence, $\epsilon = 1$ for a perfect "black body" and is between 0 and 1 for all other materials.

Wien's displacement law: $\lambda_{max}\, T = 0.0029\ \text{m} \cdot \text{K}$ – Describes the location of the wavelength peak in the black-body spectrum as a function of temperature.