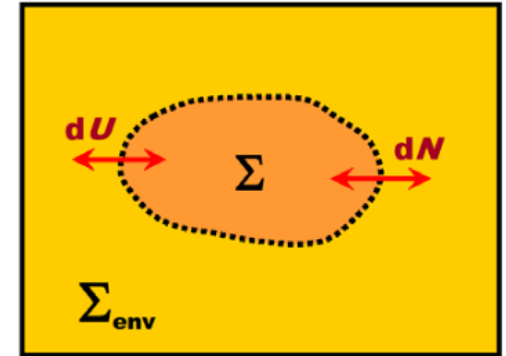# The GRAND CANONICAL ENSEMBLE

Now we go to the most general situation we will discuss, where both energy (including heat) __AND__ particles can be exchanged with the bath. Our new conditions are then

$$E_0 = \varepsilon_k + \varepsilon_j = \text{const} \quad \text{(for all allowed pairs k, j)}$$

$$N_0 = N_\alpha + n_\beta = \text{const} \quad \text{(for all allowed pairs } \alpha, \beta)$$

where N_0 is the total # of particles in "system+bath", and E_0 the total energy.

Let's clarify the notation here a bit. In the canonical ensemble, the number **n** of particles of the system was held constant – the eigenenergies ε_j of the system could then be labelled with the index **j**, without paying attention to **n**.

Now, however, we allow **n** to vary, so we label the different possible values of **n** by an index β (not to be confused with the inverse temperature). The particle number n_β then takes integer values, as does the number N_α of particles in the bath.

It then becomes clear that in general, the allowed eigenenergies of the total "system + bath" must depend on all of these parameters, ie., we have allowed energies

$$E_{\alpha\beta,kj} = \varepsilon_k(N_\alpha) + \varepsilon_j(n_\beta)$$

In what follows we simplify the notation as above, by suppressing the reference to the particle number dependence in the energy eigenstates. However, we notice that in doing sums over state for the central system we must now sum over both the indices **j** and β.

PROBABILITIES in the GRAND CANONICAL ENSEMBLE

We now find a state multiplicity of form

$$\Omega_0(\varepsilon_j, n_\beta ; \mathcal{E}_k, N_\alpha) = \Omega(\varepsilon_j, n_\beta) \Omega_{env}(\mathcal{E}_k, N_\alpha) \delta(E_0 - (\varepsilon_j + \mathcal{E}_k)) \delta(N_0 - (n_\beta + N_\alpha))$$

In exactly the same way as for the canonical ensemble, we assume that the bath is very big compared to the central system – it then follows that

$$\varepsilon_j / E_0 \ll 1 \qquad \text{and} \qquad n_\beta / N_0 \ll 1$$

Then, by the same arguments as before, the most probable state is one where the bath state has $(\mathcal{E}_k, N_\alpha) = (E_0, N_0)$, ie., the bath has all the energy and all the particles. Again, however, to find the probability of the system being in some state where it has finite energy and a finite number of particles, we must expand away from this most probable state. We then get

$$\ln \Omega_{env}(E, N) = \ln \Omega_{env}(E_0, N_0) + (d \ln \Omega_{env} / d E)\big|_{E=E_0} (E_0 - E)$$

$$+ (d \ln \Omega_{env} / d N)\big|_{N=N_0} (N_0 - N) + ..$$

$$= \ln \Omega_{env}(E_0) - \beta\varepsilon + \mu\beta n \ ....$$

where $\varepsilon = E_0 - E$ (central system energy) $\qquad n = N_0 - N$ (central system number)

We then use $dS/dN = -\mu/T$, and $S = k \ln W$, to get $d \ln \Omega / d N = -\mu/k_B T$.

Then, as before, we exponentiate to get

$$P(\varepsilon_j, n_\beta) = \exp[-\beta(\varepsilon_j - \mu n_\beta)] / \Xi \qquad \text{with} \qquad \Xi(\beta, \mu) = \sum_{j, \beta} \exp[-\beta(\varepsilon_j - \mu n_\beta)]$$

CALCULATING with the GRAND CANONICAL PARTITION FUNCTION

The grand canonical partition function, viz., $\Xi(\beta,\mu) = \sum_{j,\beta} \exp[-\beta(\varepsilon_j - \mu n_\beta)]$ is an obvious generalization of the canonical partition function (which we recall is given by $Z(\beta) = \sum_j \exp[-\beta\varepsilon_j]$).

All the usual stuff goes through – we have additivity of **ln Ξ** , and so on. The number **n** of particles is now a thermodynamic variable. We can write:

$$P(n) = \Xi^{-1}\sum \exp[\beta(n\mu - E_i)] = \Xi^{-1}\exp[\beta n\mu]\sum\exp[-\beta E_i] = \Xi^{-1}\alpha^n Z_n$$

where $\alpha \equiv \exp[\beta\mu]$ is the "activity", and Z_n is the canonical partition fn. for **n** particles. Then

$$\langle n \rangle = \Xi^{-1}\sum_{n,i} n\exp[\beta(n\mu - E_i)] = k_B T \Xi^{-1}\left(\frac{\partial\Xi}{\partial\mu}\right)_T \rightarrow \left(\frac{\partial\ln\Xi}{\partial\ln\alpha}\right)_T = \frac{\alpha}{\Xi}\left(\frac{\partial\Xi}{\partial\alpha}\right)_T$$

Likewise the energy is $\langle E \rangle = \Xi^{-1}\sum_{n,i} E_i\exp[\beta(n\mu - E_i)] = -\Xi^{-1}\left(\frac{\partial\Xi}{\partial\beta}\right)_T + \mu\langle n\rangle$

We can also calculate fluctuations. Thus, eg., we have

$$\langle n^2 \rangle = \Xi^{-1}\sum_{n,i} n^2\exp[\beta(n\mu - E_i)] = \beta^{-2}\Xi^{-1}\left(\frac{\partial^2\Xi}{\partial\mu^2}\right)_T$$

and $\langle n\rangle^2 = \left[\beta^{-1}\Xi^{-1}\left(\frac{\partial\Xi}{\partial\mu}\right)_T\right]^2$ so that finally

$$\langle \Delta n^2 \rangle = \beta^{-2}\frac{\partial}{\partial\mu}\left(\Xi^{-1}\frac{\partial\Xi}{\partial\mu}\right)_T = \beta^{-1}\left(\frac{\partial\langle n\rangle}{\partial\mu}\right)_T = \beta^{-1}\left(\frac{\partial\mu}{\partial\langle n\rangle}\right)^{-1}$$

MORAL: We do same manoeuvres as for the canonical ensemble

EXAMPLE 1. ATMOSPHERIC DENSITY: This is an old problem. We start by noting again that the chemical potential is a measure of the energy involved in adding a particle to the system. In what follows, to make things more transparent, we are going to use a hybrid argument, involving both the chemical potential and the canonical distribution.

Consider a particle of mass **m** in the earth's atmosphere. If we don't go too high above the earth, we can approximate its gravitational energy in the earth's field as

$$E = mgz$$

It then follows that the probability of finding it at height **z**, in the height interval of width **dz**, is just

$$P(z)dz = Z^{-1} \exp[-\beta mgz]dz$$

where the <u>canonical</u> partition function is just $\quad Z(\beta) = \int_0^\infty dz e^{-\beta mgz} = 1/\beta mg$

Since the particle density is proportional to the probability of finding the particle at height **z**, we also have

$$\rho(z) = \rho_0 \exp[-\beta mgz] \quad \text{so that} \quad mgz = -k_B T \ln \frac{\rho(z)}{\rho_0}$$

Now let's bring in the chemical potential. It is physically obvious (and we shall prove it later) that the sum of the gravitational energy and the chemical potential must be the same for all **z** (otherwise we could have a "perpetuum mobile"). We then must have

$$\mu(z) + mgz = \mu_0 \quad \text{so that} \quad \mu(z) = \mu_0 + k_B T \ln \frac{\rho(z)}{\rho_0}$$

This formula fails if we have really large **z**, since the gravitational potential energy is no longer linear in **z**.

EXAMPLE 2. PARTIALLY IONIZED GAS: This is another old problem – relevant to both chemistry and to astrophysics.
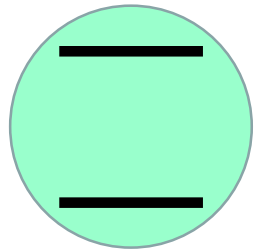
E = 0
n = 0

E = -I
n = 1

We have a toy model for an atom, in which the ground state is either occupied (with occupation n=1, and energy E = -I) or it is unoccupied (ie., ionized), with occupation n=0 and energy E=0 .

The grand canonical partition function for a single such system is then

$$\Xi = 1 + \alpha \exp[\beta I]$$

where as before the activity is defined as $\alpha \equiv \exp[\beta \mu]$

As discussed above, we can then immediately calculate the expectation value for the fraction of unionized atoms in an ensemble – it is just

$$\langle n \rangle \;\; = \;\; \frac{\alpha}{\Xi} \frac{\partial \Xi}{\partial \alpha} \;\; = \;\; \frac{\alpha \exp[\beta I]}{1 + \alpha \exp[\beta I]} \;\; = \;\; \frac{1}{\exp[-\beta(\mu + I)] + 1}$$

Note that our job is not yet finished here - this is because μ itself depends on temperature, and we have to find this dependence.

Before going on, note that for any dilute gas of these atoms, at temperature T, we can argue that they are fairly independent of each other. If this is the case then we use the same arguments as for a canonical ensemble to find that for N such atoms:

$$\Xi_N \;\; = \;\; \Xi_1{}^N$$

It then follows that for such a gas, all extensive properties will be given by multiplying the single atom result by N. Thus, the number of unionized atoms per unit volume is just ρ <n>, where ρ is the number density.

To use the expression on the previous page, we need to know how the chemical potential of a dilute gas varies with temperature. This is given by (to be proven later):

$$\mu = k_B T \ln\left[\frac{\rho}{\rho_q}\right]$$

where $\rho_q \equiv \left(\frac{m k_B T}{2\pi \hbar^2}\right)^{3/2} (2S+1)$ is the 'quantum volume' for a classical gas (here we assume each atom has spin **S**).

Some Numbers: At the surface of the sun we have $T = 6400K$ (ie., $k_B T = 0.55 eV$), and $\rho = 6 \times 10^{19} m^{-3}$

To simplify, let **S= 0**; then $\rho_q = 1.25 \times 10^{27} m^{-3}$

We then have $\mu = k_B T \ln \alpha = 0.55 eV \ln \dfrac{6 \times 10^{19}}{1.25 \times 10^{27}} = 0.55 eV \ln\left[4.8 \times 10^{-8}\right]$ = $-9.3 eV$

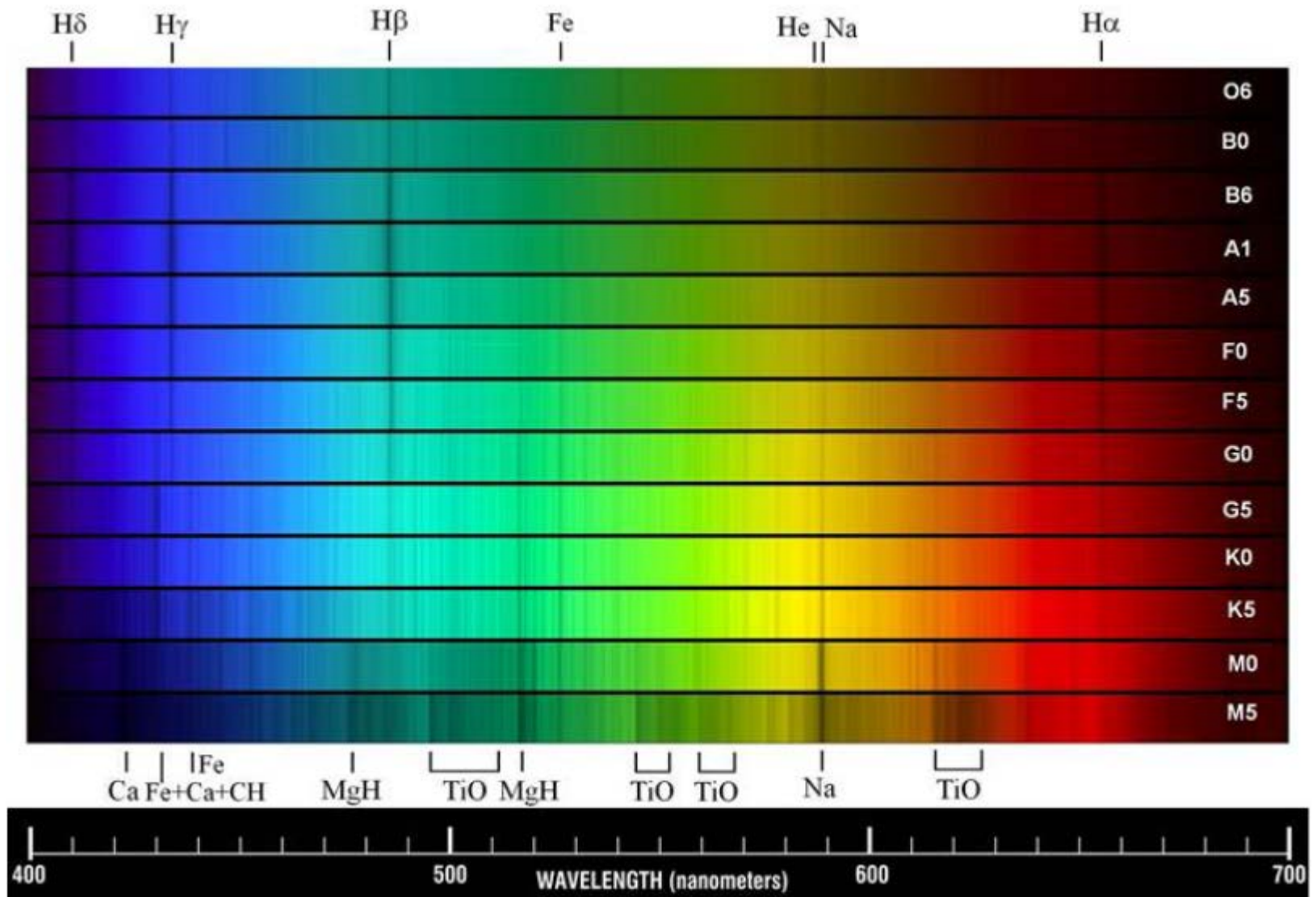Now let's consider 2 different ionic species in the sun's atmosphere.

(i) Lithium: we have $I = 5.4 eV$

so that $\langle n \rangle \approx \dfrac{1}{\exp[(9.3 - 5.4)/0.55]} = 8 \times 10^{-4}$ (almost completely ionized)
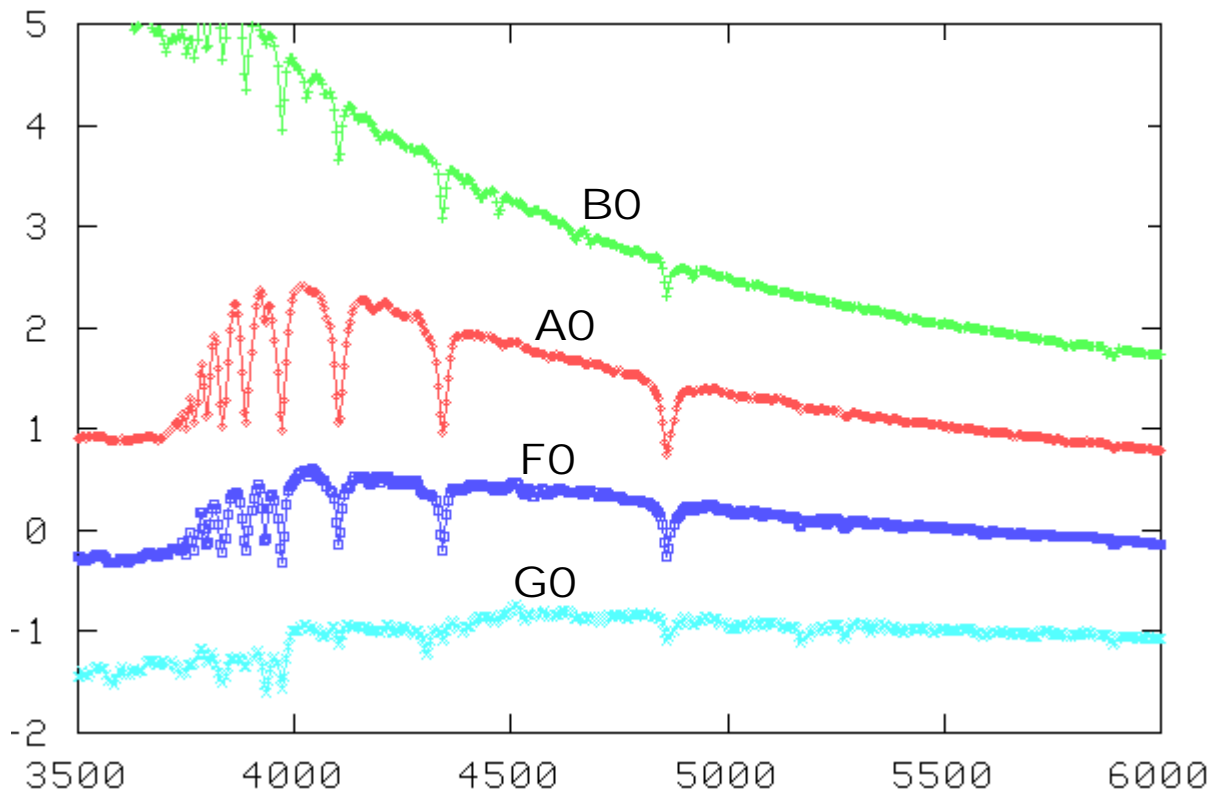
(ii) Hydrogen: now we have $I = 13.6\ eV$

which gives $<n> \sim 0.9996$ (very weakly ionized)

From this we see that the level of ionization of different species gives a fantastically sensitive measure of the physical state of the gas.

These are spectra for different stellar types, whose surface temperature varies from roughly 40,000K (type O6) down to 3,00K (type M6). The sun is type G2.

This graph plots **ln** *I* (λ) **vs** λ, **for stars of four different spectral types; here** *I* (λ) **is the intensity of radiation, and** λ **is the wavelength of the radiation. The most prominent absorption lines come from the "Balmer series' In which H atoms, already excited to the first excited level (n=2), are further excited to higher levels.**

Details are as follows:

Intensity increases extremely fast as temp. **T** goes up (Stefan-Boltzmann law); the peak intensity shifts to lower λ (higher frequency) as **T** goes up (Planck distribution)

B0: T ~ 34,000 K. The lines are weak because the density of H atoms in the n=2 state is very low - almost all H atoms are already excited to higher levels.

A0: T ~ 9,800 K. Strong Balmer absorption lines – most H atoms in the n=2 state.

F0: T ~ 7,600 K. Balmer lines weaker – most atoms now in ground state (n=1).

G0: T ~ 6,400 K. Balmer lines v. weak – almost all H atoms in ground state.