

§9. Canonical Ensemble.9.1 Gibbs Distribution

We are now going to implement the program of maximizing  $S_G$ , ~~unconstrained~~ determining the resulting probabilities  $\{p_\alpha\}$  subject to only one physical constraint: a fixed value of mean energy:

$$\sum_{\alpha} p_{\alpha} E_{\alpha} = U \quad (1)$$

The realizations of a system described by this probability distribution are called the "canonical ensemble" (introduced by J.W. Gibbs 1839-1903).

Other constraints will define different ensembles (some of which will be discussed later).

So, we want

$$S_G = - \sum_{\alpha} p_{\alpha} \ln p_{\alpha} \rightarrow \max \text{ subject to } \sum_{\alpha} p_{\alpha} E_{\alpha} = U$$

$\Downarrow$

and  $\sum_{\alpha} p_{\alpha} = 1$

$$S_G - \lambda \left( \sum_{\alpha} p_{\alpha} - 1 \right) - \beta \left( \sum_{\alpha} p_{\alpha} E_{\alpha} - U \right) \rightarrow \max$$

unconditionally

Lagrange multipliers

$$dS_G - \lambda \sum_{\alpha} dp_{\alpha} - \left( \sum_{\alpha} p_{\alpha} - 1 \right) d\lambda - \beta \sum_{\alpha} E_{\alpha} dp_{\alpha} - \left( \sum_{\alpha} p_{\alpha} E_{\alpha} - U \right) d\beta = 0$$

||

$$- \sum_{\alpha} (\ln p_{\alpha} + 1) dp_{\alpha}$$

$$-\sum_{\alpha} dp_{\alpha} (\underbrace{lp_{\alpha} + 1 + \lambda + \beta E_{\alpha}}_0) - \underbrace{(\sum_{\alpha} p_{\alpha} - 1)}_0 d\lambda - \underbrace{(\sum_{\alpha} p_{\alpha} E_{\alpha} - U)}_0 d\beta = 0$$

$$p_{\alpha} = e^{-\beta E_{\alpha} - 1 - \lambda} \rightarrow \text{(normalization)} \quad \text{find } \beta$$

$$e^{-1-\lambda} \sum_{\alpha} e^{-\beta E_{\alpha}} = 1$$

$$\text{so } e^{-1-\lambda} = \frac{1}{Z(\beta)}$$

$$(2) \quad p_{\alpha} = \frac{e^{-\beta E_{\alpha}}}{Z(\beta)}$$

Gibbs (Canonical)  
distribution

$$Z(\beta) = \sum_{\alpha} e^{-\beta E_{\alpha}} \quad (3)$$

partition function  
(Z for "Zustandssumme")

The Lagrange multiplier  $\beta$  is found from

$$U = \sum_{\alpha} p_{\alpha} E_{\alpha} = \frac{1}{Z(\beta)} \sum_{\alpha} E_{\alpha} e^{-\beta E_{\alpha}} = - \frac{\partial \ln Z}{\partial \beta} \quad (4)$$

(an implicit equation for  $\beta$  in ~~terms~~ terms of  $U$ ).

NB: Everything here is also a function of all other parameters that are viewed as exactly fixed: e.g., volume  $V$ , # of particles  $N$  - they enter via the dependence of the energy levels on them  $E_{\alpha} = E_{\alpha}(V, N)$

If these things are not fixed but rather just have some average values, different ensembles are obtained (e.g. the grand canonical ensemble, where  $\langle N \rangle$  is fixed or the so-called "pressure ensemble" where  $\langle V \rangle$  is fixed...)

## 9.2 Construction of thermodynamics

I am now going to show you that we have solved the problem posited in §7: how to calculate all thermodynamically relevant things from just knowing the energy levels  $\{E_\alpha\}$  of a given system. But for this, we first need to establish what  $\beta$  means and also how to calculate the thermodynamical entropy  $S$  and pressure  $P$ .

The Gibbs entropy for the Gibbs distribution is

$$S_G = -\sum_\alpha p_\alpha \ln p_\alpha = -\sum_\alpha \frac{e^{-\beta E_\alpha}}{Z} (-\beta E_\alpha - \ln Z) =$$

$$= \beta \underbrace{\sum_\alpha E_\alpha \frac{e^{-\beta E_\alpha}}{Z}}_{\sum_\alpha E_\alpha p_\alpha = U} + \sum_\alpha \frac{e^{-\beta E_\alpha}}{Z} \ln Z, \quad \sum_\alpha p_\alpha = 1$$

so 
$$S_G = \beta U + \ln Z \quad (5)$$

Therefore,

$$dS_G = \beta dU + \cancel{U d\beta} + \frac{dZ}{Z}$$

$$= \frac{1}{Z} \sum_\alpha e^{-\beta E_\alpha} (-\beta dE_\alpha - E_\alpha d\beta)$$

$$= -\beta \sum_\alpha p_\alpha dE_\alpha - \cancel{U d\beta}$$

$$= \beta \left( dU - \sum_\alpha p_\alpha dE_\alpha \right) \quad (6)$$

here  $E_\alpha$  is changed holding  $\{p_\alpha\}$  fixed

If  $E_\alpha = E_\alpha(V)$ , and we are changing the volume then

$$dE_\alpha = \left( \frac{\partial E_\alpha}{\partial V} \right)_{p_1, \dots, p_\Omega} dV$$

But, recalling eq. (8) of §7,

$$P = - \sum_{\alpha} p_{\alpha} \left( \frac{\partial E_{\alpha}}{\partial V} \right)_{p_1 \dots p_{\Omega}}$$

So (6) becomes

$$dS_G = \beta (dU + P dV) = \beta dQ_{rev} \quad (7)$$

↑  $dU - dW_{rev} = dQ_{rev}$  by definition of heat

This is a full differential of  $S_G$ , which is clearly a function of state, so we have found that  $\beta$  is an integrating factor of heat in th. equilibrium — Kelvin's definition of temperature!

Thus, it must be the case that

$$\beta = \frac{1}{k_B T} \quad (8)$$

{ differs from the thermodynamical temperature at most by a constant factor, which is chosen to be Boltzmann's constant simply to convert from energy units ( $[\beta] = [\text{energy}^{-1}]$ ) to Kelvin

Then (7) immediately implies that

$$S = k_B S_G \quad (9)$$

thermodynamical entropy      Gibbs entropy

NB: Technically,  
 $S = k_B S_G + \text{const}$   
 If  $T \rightarrow 0$ ,  $\beta \rightarrow \infty$  and so  $p_{\alpha} \rightarrow 0$  except for d.s.t.  $E_{\alpha} = 0$ , for which  $p_{\alpha} \rightarrow 1 \Rightarrow S_G \rightarrow 0$  (p.73)  
 So const = 0 is 3rd Law

and (7) becomes the familiar fundamental equation of thermodynamics:

$$\boxed{TdS = dU + PdV} \quad (10)$$

We are done: introducing as usual the free energy

$$F = U - TS,$$

we can calculate everything (see p.65):

$$P = - \left( \frac{\partial F}{\partial V} \right)_T, \quad S = - \left( \frac{\partial F}{\partial T} \right)_V, \quad U = F + TS$$

eqn. of state
entropy
energy

and we now have the explicit expression for  $F$  in terms of the energy levels of the system:

from (5) and (9),

$$\frac{S}{k_B} = \frac{U}{k_B T} + \ln Z$$

and so  $\boxed{F = U - TS = -k_B T \ln Z} \quad (11)$

where  $\boxed{Z = \sum_{\alpha} e^{-\beta E_{\alpha} / k_B T}$  from (3) & (8)

(12)

Thus, if we know the partition function, we know everything about our system that we need to know to describe its equilibrium thermodynamics. L2 ended here

Note a cute form in which Gibbs distribution can

be written: 
$$p_{\alpha} = \frac{e^{-\beta E_{\alpha}}}{Z} = e^{\beta(F - E_{\alpha})}$$

$\uparrow$   $e^{-\beta F}$  from (11)

P.S. If you did not believe the derivation of eqs (8) & (9),  
here is a more formal proof (Schrodinger Ch. 11)

We had derived, using only the principle of max. entropy  
(Gibbs entropy!) ~~and~~ and the definition of pressure:

$$dS_G = \beta dQ_{rev} \quad (7)$$

From thermodynamics, we knew that

$$dS = \frac{1}{T} dQ_{rev} \quad (13)$$

$$\text{Therefore, } dS = \frac{1}{\beta T} dS_G \quad (14)$$

LHS is a full differential  $\Rightarrow$  so is the RHS

$$\Rightarrow \frac{1}{\beta T} = f(S_G) \text{ a function of } S_G \text{ only} \quad (15)$$

$$dS = f(S_G) dS_G \quad (16)$$

Integrate:  $S = \varphi(S_G)$  some function of  $S_G$  ~~(17)~~ (17)

But  $S$  is an additive function and so is  $S_G$   
 $\uparrow$  know from thermo.  $\uparrow$  will prove shortly

Therefore, for two systems, 1 & 2, we have

$$\left\{ \begin{array}{l} S_{G1} + S_{G2} = S_{G12} \leftarrow \text{combined system} \\ S_1 + S_2 = S_{12} \\ \varphi_1(S_{G1}) + \varphi_2(S_{G2}) = \varphi_{12}(S_{G1} + S_{G2}) \\ \varphi_1'(S_{G1}) = \varphi_{12}'(S_{G1} + S_{G2}) \\ \varphi_2'(S_{G2}) = \varphi_{12}'(S_{G1} + S_{G2}) \end{array} \right.$$

Therefore,  $\varphi_1'(S_{G1}) = \varphi_2'(S_{G2}) = \text{const} \equiv k_B$   
 So  $\varphi'(S_G) = f(S_G) = k_B$  "separation const"

$$\Downarrow$$

From (15),  $\frac{1}{\beta T} = k_B \Rightarrow \boxed{\beta = \frac{1}{k_B T}} \quad (8)$

From (16),  $dS = k_B dS_G$

$$\Downarrow$$

$$\boxed{S = k_B S_G + \text{const}} \quad (18) \quad \boxed{9.4 \text{ 3rd Law.}}$$

Let's discuss in more detail than we did on p. 81 the choice  $\text{const} = 0$  ( $\Rightarrow S = k_B S_G$  (9)).

From (5), we have

$$S_G = \ln \sum_{\alpha} e^{-\beta E_{\alpha}} + \beta \frac{\sum_{\alpha} E_{\alpha} e^{-\beta E_{\alpha}}}{\sum_{\alpha} e^{-\beta E_{\alpha}}}$$

Consider what happens when  $T \rightarrow 0$ , or  $\beta \rightarrow \infty$ .

Suppose the lowest energy level is  $E_1$  and  $\alpha = 1, \dots, m$  microstates have this energy (so  $E_{\alpha} > E_1$  for  $\alpha > m$ )

Then  $S_G = \ln \left( m e^{-\beta E_1} + \sum_{\alpha=m+1}^{\infty} e^{-\beta E_{\alpha}} \right) + \beta \frac{m E_1 e^{-\beta E_1} + \sum_{\alpha>m} E_{\alpha} e^{-\beta E_{\alpha}}}{m e^{-\beta E_1} + \sum_{\alpha>m} e^{-\beta E_{\alpha}}}$

$$= \ln m e^{-\beta E_1} \left( 1 + \sum_{\alpha>m} e^{-\beta(E_{\alpha}-E_1)} \right) + \beta E_1 \frac{1 + \sum_{\alpha>m} \frac{E_{\alpha}}{E_1} e^{-\beta(E_{\alpha}-E_1)}}{1 + \sum_{\alpha>m} e^{-\beta(E_{\alpha}-E_1)}}$$

$$\approx \ln m - \beta E_1 + \frac{1}{m} \sum_{\alpha>m} e^{-\beta(E_{\alpha}-E_1)} + \beta E_1 \left[ 1 + \sum_{\alpha>m} \left( \frac{E_{\alpha}}{E_1} - 1 \right) e^{-\beta(E_{\alpha}-E_1)} \right] + \dots$$

$$= \ln m + \sum_{\alpha > m} e^{-\beta(E_\alpha - E_1)} \left[ \beta(E_\alpha - E_1) + \frac{1}{m} \right] + \dots$$

$\uparrow$   
 $\beta \rightarrow \infty$ , this exp'ly small  
 factor kills everything

Thus,  $\boxed{S_G \rightarrow \ln m \text{ as } T \rightarrow 0}$  (19)

$\uparrow$   
 degeneracy of the lowest energy level

Setting const = 0 in (18) means that

$$S \rightarrow k_B \ln m \text{ as } T \rightarrow 0 \quad (20)$$

for the thermodynamical entropy.

Recall that the 3<sup>rd</sup> law said  $S \rightarrow 0$  as  $T \rightarrow 0$ .

This is OK, because  $k_B \ln m$  is very small compared to values that matter (since  $S$  is additive, it will generally be proportional to the # of particles in the system, so  $S \sim k_B N$  and obviously,  $\ln m \ll N$  except for very strange systems).

[see further discussion in Schrödinger Ch. III]

In any event, these details don't matter very much because what is important is that the const in (18) is a const, independent of the parameters of the system, so all entropy differences are independent of it - and related by  $k_B$  for  $S$  and  $S_G$ .