PHY2023 Supplement 2: Lagrange Undetermined Multipliers (non-examinable).

We require to maximise

$$\Omega = \frac{N!}{\prod_{i=0}^{\infty} n_i!}$$

subject to the constraints $\sum_{i=0}^{\infty} n_i = N \quad \sum_{i=0}^{\infty} n_i \, \varepsilon_i = U$

Firstly, note that maximising Ω is equivalent to maximising lnΩ, hence we wish to maximise

$$\ln \Omega = \ln N! - \sum_{i=0}^{\infty} \ln n_i!$$

Secondly, note that for any realistic system N and all the n_i's will be very large, so we can apply the following approximation

$$\ln x! \cong x \ln x - x \text{ (for large } x\text{, “Stirling's approximation”)}$$

[This approximation is very widely used in statistical mechanics, so should be learnt. See Mandl or the 'Supplementary 3' sheet for more details.]

Combining these results, we wish to maximize

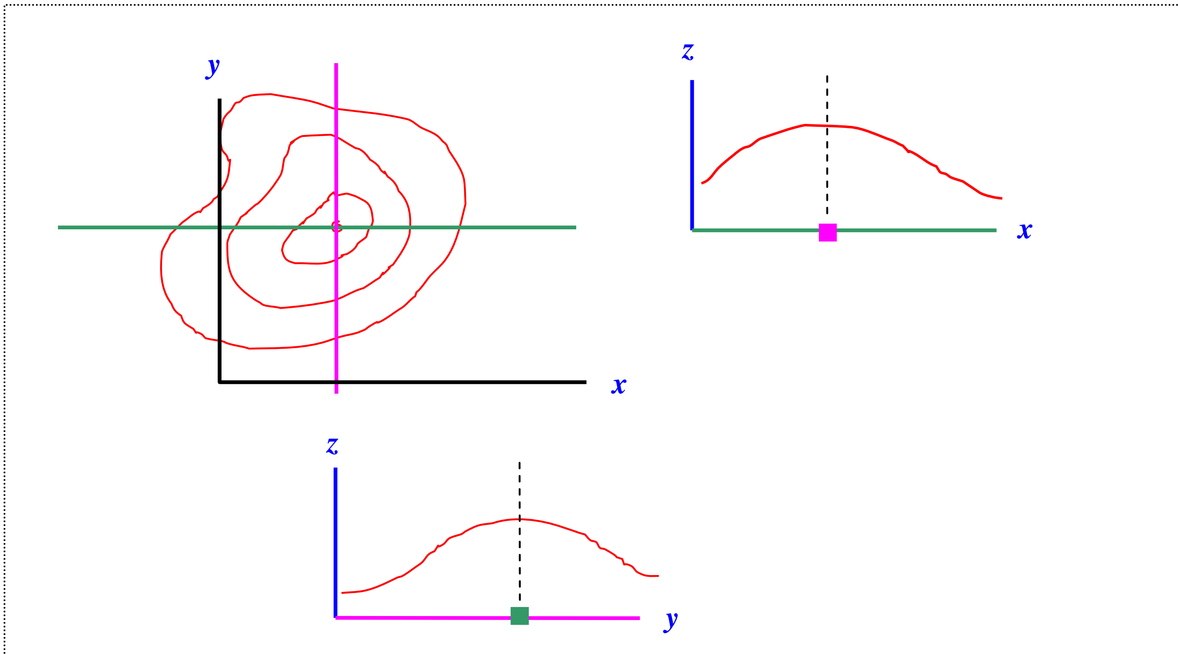
$$\begin{aligned}
\ln \Omega &\cong N \ln N - N - \sum_{i=0}^{\infty} \left(n_i \ln n_i - n_i\right) \\
&\cong N \ln N - N - \sum_{i=0}^{\infty} n_i \ln n_i + \sum_{i=0}^{\infty} n_i \\
&\cong N \ln N - \sum_{i=0}^{\infty} n_i \ln n_i
\end{aligned}$$

(since $N = \sum_{i=0}^{\infty} n_i$).

subject to the constraints $\sum_{i=0}^{\infty} n_i = N \quad \sum_{i=0}^{\infty} n_i \, \varepsilon_i = U$.

Although the minimum possible change in any n_i is 1, since n_i is itself extremely large i.e. $\delta n_i << n_i$, we can effectively consider that it is possible to perturb any n_i by an infinitesimally small amount dn_i. Our problem is thus to find the values of n_i that yield <u>no change in lnΩ to first order</u>, when any n_i is perturbed by dn_i. Compare this to finding the maximum of a function $y(x)$; we seek a value of x that causes no change in y to first order when x is perturbed by dx i.e. we seek $dy/dx = 0$. Our problem is similar, except that lnΩ is a function of many variables (all the n_i's). Consider locating the maximum of a function of 2 variables, e.g. finding the highest point on a surface $z(x,y)$. The maximum (or minimum) is the point that satisfies

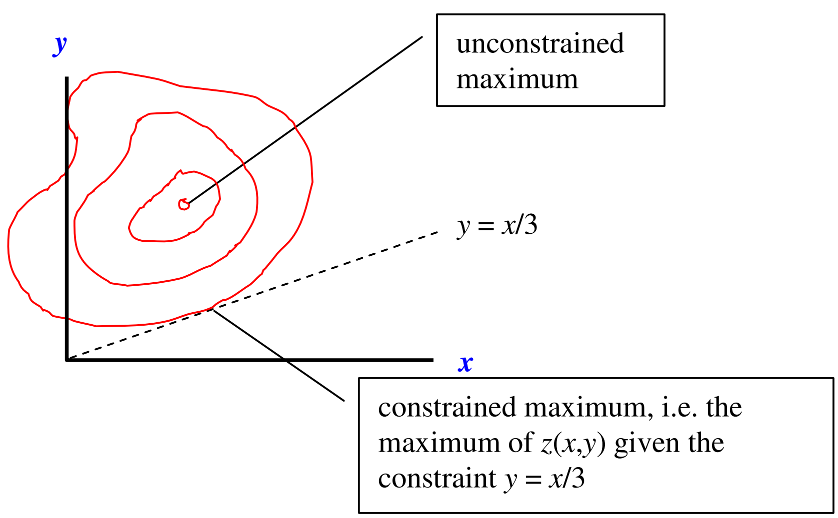
$$\frac{\partial z}{\partial x} = \frac{\partial z}{\partial y} = 0$$



Hence we seek the n_i's that satisfy

$$\frac{\partial \ln \Omega}{\partial n_i} = 0 \quad \forall\, i = 0 \ldots \infty \;\; \underline{\text{subject to the constraints}} \;\; \sum_{i=0}^{\infty} n_i = N \quad \sum_{i=0}^{\infty} n_i\, \varepsilon_i = U \, .$$

In the figure above, the intersection of the pink and green lines is the <u>unconstrained</u> maximum of the function $\underline{z}(x,y)$. A constrained maximum would be the maximum value of z, given that some relation must also exist between x and y. e.g. if the constraint is that $y = x/3$ then the constrained maximum is the largest value of z that can be found lying along the line $y = x/3$:-



To find the maximum of $z(x,y)$ satisfying $y = x/3$, express the constraint equation as $3y - x = 0$ and invent a new function

$$\Gamma(x, y, \lambda) = z(x, y) - \lambda(3y - x)$$

i.e. a function of 3 variables, x, y and λ, where λ is an "undetermined multiplier". Consider locating an <u>unconstrained</u> maximum of this function. This is a point at which

$$\frac{\partial\Gamma(x, y, \lambda)}{\partial x} = \frac{\partial\Gamma(x, y, \lambda)}{\partial y} = \frac{\partial\Gamma(x, y, \lambda)}{\partial\lambda} = 0$$

Since $\dfrac{\partial\Gamma(x, y, \lambda)}{\partial\lambda} = -(3y - x)$, an unconstrained maximum of Γ must be a set of values (x,y,λ) where x and y <u>automatically</u> satisfy our constraint equation. Also, since at any point satisfying the constraint equation we must have $\Gamma(x,y,\lambda) = z(x,y)$ it follows that since we cannot find a larger value of Γ for any (x,y,λ) we also cannot find a larger value of $z(x,y)$ where x and y also satisfy our constraint equation. The problem of finding a constrained maximum of a function is thus reduced to finding a conventional unconstrained maximum of a modified function. Further constraints can be added by introducing more undetermined multipliers and supplementing Γ with the additional constraint equations.

Applying this idea to our original problem, we seek an unconstrained maximum of
$\Gamma = \ln\Omega - \lambda\left(\sum_{i=0}^{\infty} n_i - N\right) - \beta\left(\sum_{i=0}^{\infty} n_i\varepsilon_i - U\right)$ w.r.t. all the n_i's, λ and β.
i.e. applying our approximate form for $\ln\Omega$ we seek to maximise

$$\Gamma = N\ln N - \sum_{i=0}^{\infty} n_i \ln n_i - \lambda\left(\sum_{i=0}^{\infty} n_i - N\right) - \beta\left(\sum_{i=0}^{\infty} n_i\varepsilon_i - U\right)$$

Let us concentrate on maximising Γ w.r.t the n_i's. We thus require the gradient of Γ to vanish w.r.t all of the n_i's simultaneously. Noting that N and U are constants, this requires

$\dfrac{\partial(n_i \ln n_i + \lambda n_i + \beta n_i\varepsilon_i)}{\partial n_i} = 0 \quad \forall n_i,$ hence
$1 + \ln n_i + \lambda + \beta\varepsilon_i = 0 \quad \forall n_i.$ Rearranging, yields for <u>each</u> n_i the relation
$\ln n_i = -(1 + \lambda) - \beta\varepsilon_i$, hence
$n_i = \exp(-(1 + \lambda))\exp(-\beta\varepsilon_i)$
i.e. n_i decreases exponentially as the energy of the corresponding level ε_i increases.

Note that at this point the multipliers λ and β remain to be determined. This can be done by applying our constraint equations. e.g. since $\sum_{i=0}^{\infty} n_i = N$ we have

$$\sum_{i=0}^{\infty} n_i = \sum_{i=0}^{\infty} \exp(-(1+\lambda))\exp(-\beta\varepsilon_i) = \exp(-(1+\lambda))\sum_{i=0}^{\infty} \exp(-\beta\varepsilon_i) = N,$$

hence $\exp\left(-\left(1+\lambda\right)\right)=\dfrac{N}{\sum_{i=0}^{\infty}\exp\left(-\beta\varepsilon_i\right)}$,

leading to $n_i=\dfrac{N\exp\left(-\beta\varepsilon_i\right)}{\sum_{i=0}^{\infty}\exp\left(-\beta\varepsilon_i\right)}$ i.e.

$$\boxed{\frac{n_i}{N}=\frac{\exp\left(-\beta\varepsilon_i\right)}{\sum_{i=0}^{\infty}\exp\left(-\beta\varepsilon_i\right)}}$$