Derivation of Boltzman distribution

With Partition function

BOLTZMANN STATISTICS أحصائية بولتزمان

توزيـع التوازن لنضام N من الجسيمات المتمايزه غير المتفاعله

تخضع للمحددات ☛ $\sum_{j=1}^{n} N_j = N$ and $\sum_{j=1}^{n} N_j \varepsilon_j = U$

عدد الطرق التي تتوزع بها الجسيمات N_1 من العدد الكلي N لتكون في المستوى $j = 1$

$$\begin{pmatrix} N \\ N_1 \end{pmatrix} = \frac{N!}{N_1!(N - N_1)!}$$

عدد الطرق التي تتوزع بها الجسيمات N_1 من العدد الكلي N أذا كان الأنحلال في مستويات الطاقه g_1 لكل جسيم هنالك أمكانيه $(g_1)^{N_1}$

$$\begin{pmatrix} N \\ N_1 \end{pmatrix} = \frac{N! g_1^{N_1}}{N_1!(N - N_1)!}$$

For $j = 2$ ☛ same situation

except that there are only $(N - N_1)$ particles remaining to deal with

$$\frac{(N - N_1)!g_2^{N_2}}{N_2!(N - N_1 - N_2)!}$$

Continuing process ↴

$$\omega_{\mathrm{B}}(N_1, N_2, N_n) = \frac{N!g_1^{N_1}}{N_1!(N - N_1)!} \times \frac{(N - N_1)!g_2^{N_2}}{N_2!(N - N_1 - N_2)!}$$

$$\times \frac{(N - N_1 - N_2)!g_3^{N_3}}{N_3!(N - N_1 - N_2 - N_3)!} \cdots$$

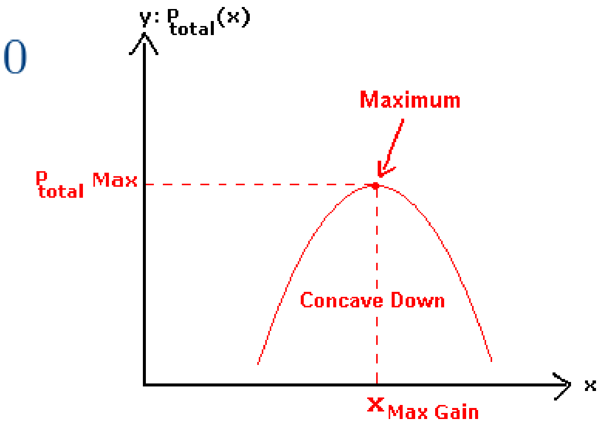
$$= N!\frac{g_1^{N_1} g_2^{N_2} g_3^{N_3} \cdots}{N_1!N_2!N_3! \cdots} = N! \prod_{j=1}^{n} \frac{g_j^{N_j}}{N_j!}$$

LAGRANGE MULTIPLIERS مضاعفات لاكرانج

Maximization of $f(x,y)$ subject to constraint $\phi(x,y) = \text{constant}$

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy = 0$$

If dx and dy were independent ☛ $\frac{\partial f}{\partial x} = \frac{\partial f}{\partial y} = 0$



$$d\phi = \frac{\partial \phi}{\partial x}dx + \frac{\partial \phi}{\partial y}dy = 0$$

$$\frac{\partial f/\partial x}{\partial \phi/\partial x} = \frac{\partial f/\partial y}{\partial \phi/\partial y}$$

For constant ratio

$$\frac{\partial f}{\partial x} + \alpha\frac{\partial \phi}{\partial x} = 0 \quad \text{and} \quad \frac{\partial f}{\partial y} + \alpha\frac{\partial \phi}{\partial y} = 0$$

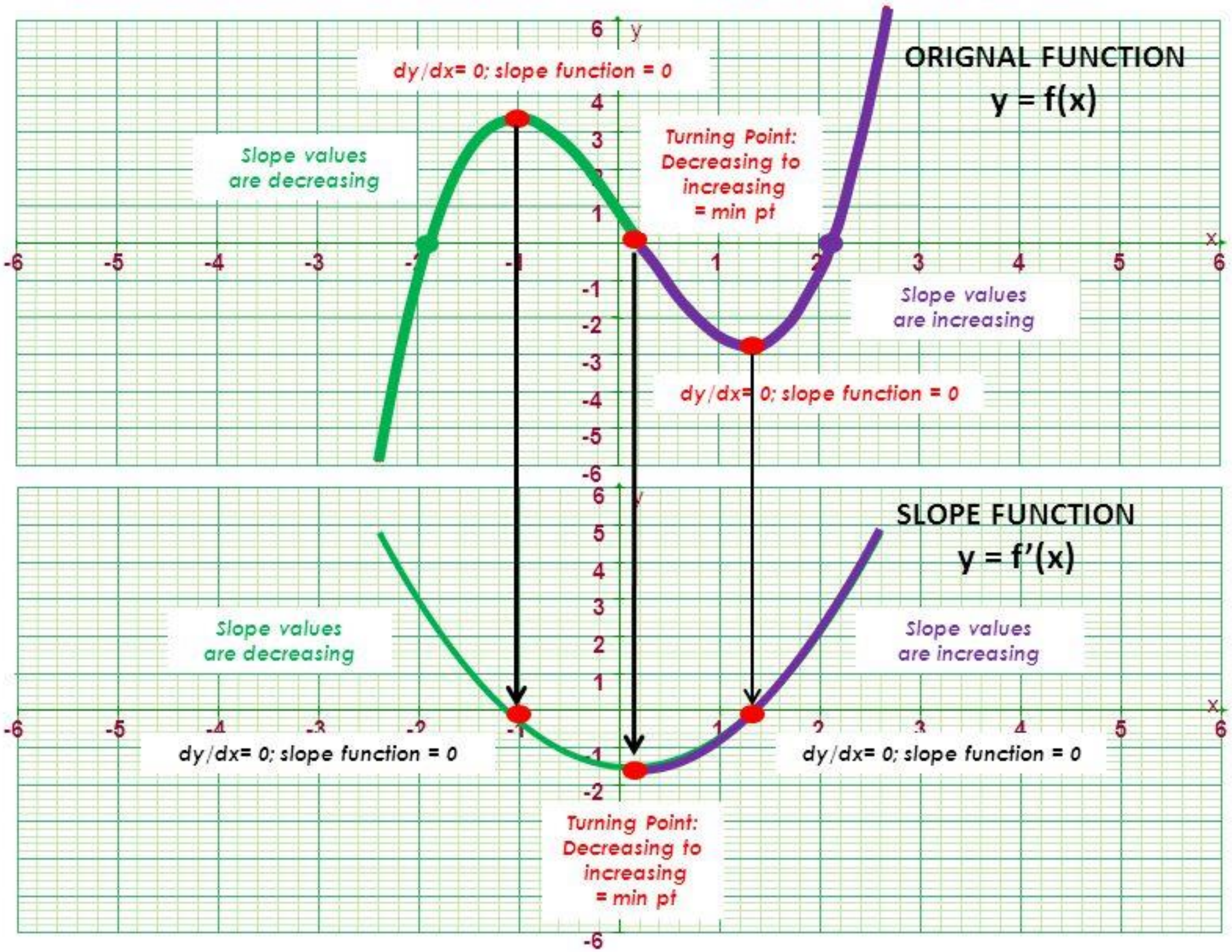
expressions we would get if we attempt to maximize $f + \alpha\phi$ without constraint

For n variables and two constraint relations

$$\frac{\partial f}{\partial x_i} + \alpha\frac{\partial \phi}{\partial x_i} + \beta\frac{\partial \psi}{\partial x_i} = 0, \qquad i = 1, 2, 3 \cdots n$$

A step further to investigate the tangents of the slope function.

Second Derivative Function is… $f''(x)$ is… d^2y/dx^2 is…



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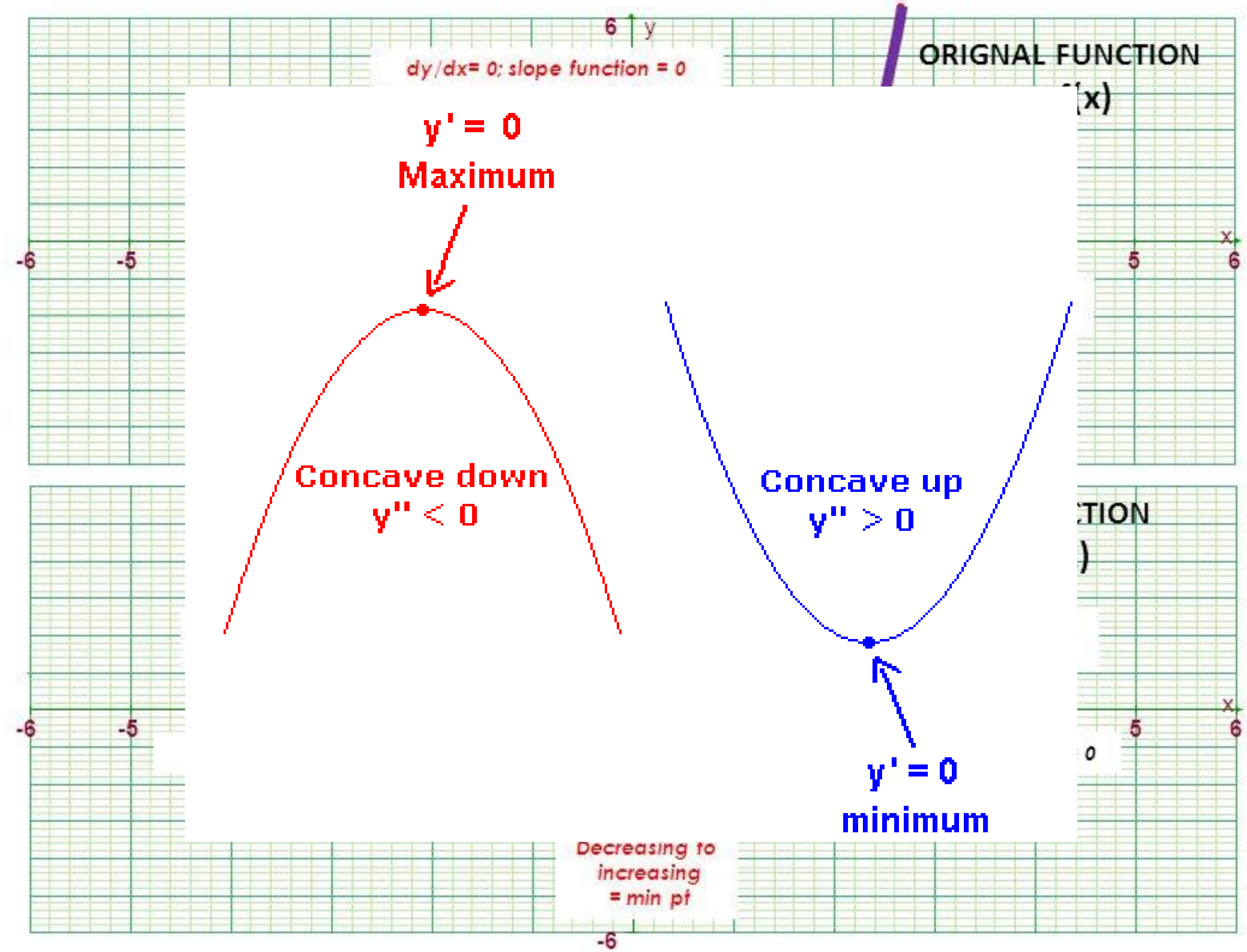

Task ☛ find maximum of $\omega_{\rm B}$ with respect to all N that satisfy constraints

In practice ☛ more convenient to maximize $\ln \omega$ than w itself

$$\ln \omega = \ln N! + \sum_{i=1}^{n} N_i \ln g_i - \sum_{i=1}^{n} \ln N_i!$$

We are concerned with $N_i \gg 1$ ☛ use Stirling's asymptotic expansion

$$\ln N! \simeq N \ln N - N + \ln \sqrt{2\pi N} + \cdots$$

Neglecting relatively small last term in (41)

$$\ln \omega = \ln N! + \sum_{i=1}^{n} N_i \ln g_i - \sum_{i=1}^{n} N_i \ln N_i + \sum_i N_i$$

Search for maximum of target function using Lagrange multipliers ↴

$$\frac{\partial}{\partial N_j} \left[\sum_i N_i \ln g_i - \sum_i N_i \ln N_i + \sum_i N_i \right] + \alpha \frac{\partial}{\partial N_j} \left(\sum_i N_i \right) + \beta \frac{\partial}{\partial N_j} \left(\sum_i N_i \varepsilon_i \right) = 0$$

In working out the derivatives ☛ only contribution comes from terms with $j = i$

$$\ln g_j - \ln N_j \underbrace{-\frac{N_j}{N_j} + 1}_{=0} + \alpha + \beta\varepsilon_j = 0$$

For every energy level

# of particles per quantum state for equilibrium of the system

$$\frac{N_j}{g_j} = e^{\alpha + \beta\varepsilon_j} = f_j(\varepsilon_j)$$

Constants α and β are related to physical properties of the system

Multiply by N_j and sum over j

$$\sum_j N_j \ln g_j - \sum_j N_j \ln N_j + \alpha \sum_j N_j + \beta \sum_j N_j \varepsilon_j = 0$$

$$\sum_j N_j \ln g_j - \sum_j N_j \ln N_j = -\alpha N - \beta U$$

Substituting ☛ $\ln \omega = \ln N! + N - \alpha N - \beta U$

simplifying ☛ $\ln \omega = C - \beta U$

Identification with Boltzmann entropy yields ☛ $S = k \ln \omega = S_0 - k\beta U$

From classical theory ☛ $dS = \frac{dU}{dT} + \frac{PdV}{T} = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$

giving ☛ $\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$

From (47) ☛ $\left(\frac{\partial S}{\partial U}\right)_V = -k\beta$

giving ☛ $\beta = -\frac{1}{kT}$

Constancy of V is ☛ because $\epsilon_j \propto V^{-2/3}$

PARTITION FUNCTION دالة التجزئه

Substituting ☛ $N_j = g_j e^{\alpha} e^{-\varepsilon_j/kT}$

so α can be easily found from ☛ $N = \sum_j N_j = e^{\alpha} \sum_j g_j e^{-\varepsilon_j/kT}$

$$e^{\alpha} = \frac{N}{\sum_j g_j e^{-\varepsilon_j/kT}}$$

Boltzmann distribution becomes ☛ $f_j = \frac{N_j}{g_j} = \frac{N\ e^{-\varepsilon_j/kT}}{\sum_j g_j e^{-\varepsilon_j/kT}}$

partition function (German Zustandssumme)

$$Z \equiv \sum_{j=1}^{n} g_j e^{-\epsilon_j/kT}$$