114036 - Statistical and Thermal Physics

Amit Keren

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Abstract

1 Introduction

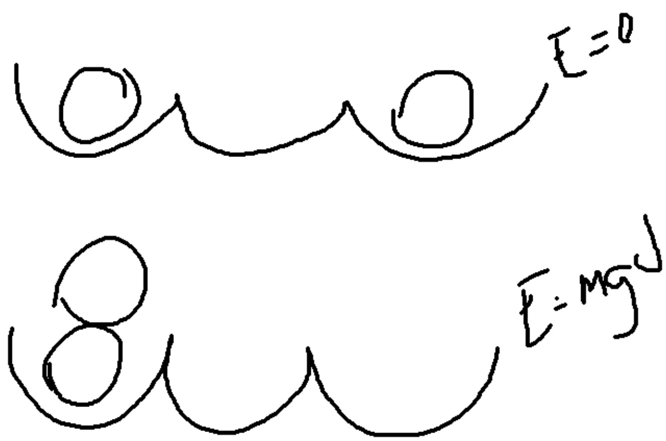
History

- First, thermodynamics was developed, before atoms were known to exist.
- Statistical physics.
- Quantum physics.

In the course, the order is the opposite.

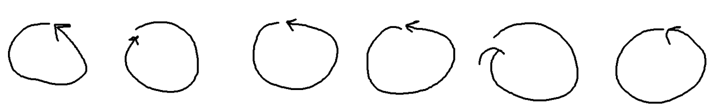
1.1

Suppose we have two balls of diameter d. If both are on the bottom, total energy is 0. If one i son the other, total energy is mgd.



Number of state	Degeneracy	Energy
0	3	0
1	3	mgd
2	0	$2mgd$

Paramagnetism Define magnetic moment as $\vec{m} = I\vec{a}$. For magnetic filed energy is $U = -\vec{B} \cdot \vec{m} = -\vec{B}\vec{\mu}$.
Suppose we a have a system of a big amount of current loops, each of which can have one of two directions - clockwise or counterclockwise. For example



To calculate total magnetic momentum we just sum all of the moments, which are either μ or $-\mu$. In upper example, $M = \sum_i \mu_i = 2\mu$.
The total number of possible states is 2^N. The possible energy is $M = (N - 2N_d)\mu$ where N_d is number of down-facing loops of current. Number of different states with sam energy is

$$\binom{N}{N_d} = \frac{N!}{N_d! N_u!}$$

Now, for even N, define

$$2S = N_u - N_d$$

Then

$$\binom{N}{N_d} = \frac{N!}{((\frac{1}{2}N - S)!((\frac{1}{2}N + S)!}$$

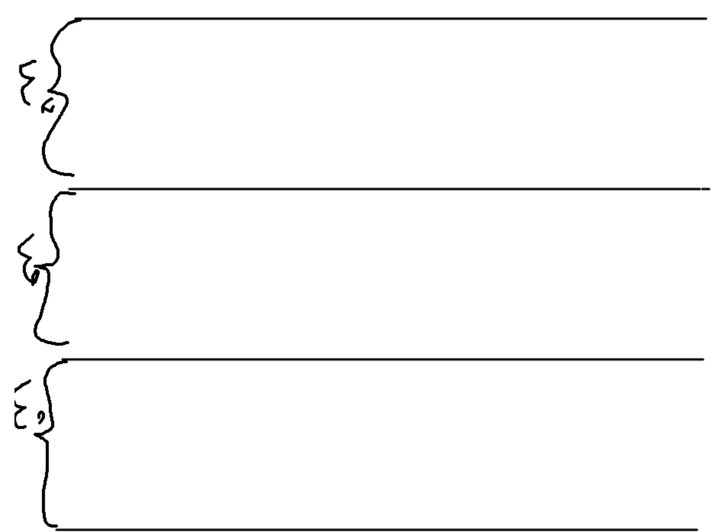
and the energy

$$U = -2S\mu B \Rightarrow S = -\frac{U}{2\mu B}$$

The degeneracy of the state thus is

$$g(N,S) = \frac{N!}{\left(\frac{1}{2}N - \frac{U}{2\mu B}\right)!(\left(\frac{1}{2}N + \frac{U}{2\mu B}\right)!}$$

Particles on shelves (quantum oscillator) Suppose we have equally-distant shelves, and energy distance between two shelves is ϵ_0:



Define $n = \frac{U}{\epsilon_0}$ which is amount of energy we have (it comes in quantas is degeneracy? What is degeneracy? It is combinations of$N$ out n with returns:

$$g(N,u) = \frac{(n+N-1)!}{n!(N-1)!} = \frac{\left(N + \frac{U}{\epsilon_0} - 1\right)!}{\left(\frac{U}{\epsilon_0}\right)!(N-1)!}$$

Particles on shelves with quadratic distances (particles in box) Now suppose distances goes as square of number opf shelve (ϵ_0, $4\epsilon_0$, ...). This problem doesn't have analytical solution. But we can find solution manually. For example, to find $g(6, 18\epsilon_0)$. The only option is 2 boxes on first energy level $U = \epsilon_0$ and 4 on second energy level, thus

$$g(6, 18\epsilon_0) = \binom{6}{2} = 15$$

1D box with particles Now we want to calculate kinetic energy:

$$E = \frac{p^2}{2m}$$

Since we can't do much with continuous values (there is infinite number of options), lets divide both momentum and position into discrete intervals of size w and l correspondingly. Now, the position is independent on energy, but there are only two options for momentum - $\pm\sqrt{2mE}$. Thus degeneracy is

$$g(1, E) = 2\frac{L}{l}$$

2D box We now divide position in momentum into intervals of length l and w in both directions. Position is still arbitrary, and momentum lies on a circle of radius $2mE$. However, its hard to calculate.
Lets define instead $S(1, E)$ - number of states with energy *less* than U. For 1-dimensional case

$$S(1, E) = \frac{L}{l} \cdot 2 \cdot \frac{\sqrt{2mE}}{w} = \frac{1}{lw} \int_{-\frac{L}{2}}^{\frac{L}{2}} ds \int_{-\sqrt{2mE}}^{\sqrt{2mE}} ds$$

In 2D we get, for box of area A

$$S(1, E) = \frac{A}{l^2} \cdot \frac{2\pi mE}{w^2} = \frac{1}{l^2 w^2} \int_{-\frac{L}{2}}^{\frac{L}{2}} dx \int_{-\frac{L}{2}}^{\frac{L}{2}} dy \iint\limits_{|p|<\sqrt{2mE}} d^2p$$

$$S(1, E) = \frac{V}{l^3} \cdot \frac{4\pi(2mE)^{\frac{3}{2}}}{3w^3}$$

We denote $h = lw$. Now note that $G(n, U) = \frac{\partial S(n,U)}{\partial U}$.

Two distinguishable particles in 1D While positions are independent, there is dependence between p_1 and p_2:

$$\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + E$$

We can note that

$$S_{2D}(1, U) = S_{1D}(2, U)$$

N particles in D dimensions

$$S_D(N, U) = \frac{1}{h^{DN}} \int\limits_{\vec{\mathbf{x}}_1 \in V} \mathrm{d}^D x_1 \ldots \int\limits_{\vec{\mathbf{x}}_n \in V} \mathrm{d}^D x_n \int\limits_{\sum_{i=1}^{n} \vec{\mathbf{p}}_i^2 \leq 2mU} \cdots \int \mathrm{d}^D p_1 \ldots \mathrm{d}^D p_n$$

Ball volume in dimension d Define gamma function. For $\alpha > 0$

$$\frac{1}{\alpha} = \int_0^\infty \mathrm{d}x\, e^{-x\alpha}$$

Differentiating n times by α (and dividing by $(-1)^n$:

$$\frac{N!}{\alpha^{N+1}} = \int_0^\infty \mathrm{d}x\, x^N e^{-x\alpha}$$

By substituting $\alpha = 1$:

$$N! = \int_0^\infty \mathrm{d}x\, x^N e^{-x}$$

Thus define

$$\Gamma(N+1) = \int_0^\infty \mathrm{d}x\, x^n e^{-x}$$

Define area of d-dimensional sphere of radius R as

$$A_d = S_d \cdot R^{d-1}$$

Define also

$$I_d = \left(\int_{-\infty}^{\infty} \mathrm{d}x\, e^{-x^2}\right)^d$$

On one hand $I_D = \pi^{\frac{d}{2}}$, on the other hand

$$I_d = \int_{-\infty}^{\infty} \mathrm{d}x_1\, e^{-x^2} \int_{-\infty}^{\infty} \mathrm{d}x_2\, e^{-x^2} \ldots \int_{-\infty}^{\infty} \mathrm{d}x_n\, e^{-x^2} = \int_{-\infty}^{\infty} \mathrm{d}x_1\, \mathrm{d}x_2 \ldots \mathrm{d}x_n\, e^{-\sum_{i=1}^{n} x_i^2}$$

For $R = \sum_{i=1}^{n} x_i^2$:

$$I_D = \int_0^{\infty} \mathrm{d}R\, S_d R^{d-1} e^{-R^2}$$

(Note that when we perform integral over angular dimensions we acquire exactly S_d from Jacobean).
For $y = R^2$, $\mathrm{d}y = 2R\,\mathrm{d}R$:

$$\int_0^{\infty} \frac{dy}{2\sqrt{y}} S_d y^{\frac{d-1}{2}} e^{-y} = \frac{S_d}{2} \int_0^{\infty} y^{\frac{d}{2}-1} e^{-y} dy = \frac{S_d}{2} \Gamma\left(\frac{d}{2}\right)$$

Thus

$$\frac{S_d}{2} \Gamma\left(\frac{d}{2}\right) = \pi^{\frac{d}{2}}$$

i.e.

$$S_d = \frac{2\pi^{\frac{d}{2}}}{\Gamma\left(\frac{d}{2}\right)}$$

Now the volume of d-dimensional ball

$$V_d = \int_0^R \mathrm{d}r\, \frac{2\pi^{\frac{d}{2}}}{\Gamma\left(\frac{d}{2}\right)} r^{d-1} = \frac{\pi^{\frac{d}{2}}}{\Gamma\left(\frac{d}{2}\right)} \frac{r^d}{\frac{d}{2}} = \frac{\pi^{\frac{d}{2}} r^d}{\Gamma\left(\frac{d}{2}+1\right)}$$

Back to our particles:

$$S_D(N,U) = \frac{1}{h^{DN}} \int_{\vec{\mathbf{x}}_1 \in V} \mathrm{d}^D x_1 \ldots \int_{\vec{\mathbf{x}}_n \in V} \mathrm{d}^D x_n \underbrace{\int \cdots \int}_{\sum_{i=1}^{n} \vec{\mathbf{p}}_i^2 \leq 2mU} \mathrm{d}^D p_1 \ldots \mathrm{d}^D p_n = \frac{L^{DN} \pi^{\frac{DN}{2}} (2mU)^{\frac{DN}{2}}}{h^{DN} \Gamma\left(\frac{DN}{2}+1\right)} = \left(\frac{L}{h}\right)^{DN} \frac{(2\pi m w)^{\frac{DN}{2}}}{\Gamma\left(\frac{DN}{2}+1\right)}$$

Thus in our world

$$S_3(N,U) = \frac{V^N \pi^{\frac{3N}{2}} (2mU)^{\frac{3N}{2}}}{h^{3N} \Gamma\left(\frac{3N}{2}+1\right)}$$

And

$$G_3(N,U) = \frac{\partial S_3(N,U)}{\partial U} = \frac{V^N \pi^{\frac{3N}{2}} (2mU)^{\frac{3N}{2}-1} \cdot \frac{3}{2} N \cdot 2m}{h^{3N} \Gamma\left(\frac{3N}{2}+1\right)} = \frac{3 V^N \pi^{\frac{3N}{2}} (2mU)^{\frac{3N}{2}-1} m N}{h^{3N} \Gamma\left(\frac{3N}{2}+1\right)}$$

Integral approximation with steepest descent Suppose we want calculate

$$I = \int \mathrm{d}x\, e^{N\phi(x)}$$

for some big N and x_{max} is maximum of ϕ:

$$I \approxeq \int \mathrm{d}x \exp\left[N\left(\phi(x_{max}) - \frac{1}{2}\left|\phi''(x_{max})\right|(x - x_{max})^2 + \frac{1}{3!}\phi'''(x_{max})(x - x_{max})^3\right)\right]$$

Then, substituting $y = \sqrt{N}(x - x_{max})$

$$I = e^{N\phi(x_{max})} \int \frac{\mathrm{d}y}{\sqrt{N}} e^{-\frac{1}{2}|\phi''(x_{max})|y^2 + \frac{1}{3!}\phi'''(x_{max})\frac{y^3}{\sqrt{N}}}$$

Since N is big, $\frac{1}{3!}\phi'''(x_{max})\frac{y^3}{\sqrt{N}}$ is negligible (and higher orders too):

$$I = e^{N\phi(x_{max})} \sqrt{\frac{2\pi}{N|\phi''(x_{max})|}}$$

Example Lets approximate $n!$:

$$\Gamma(n+1) = \int_0^\infty \mathrm{d}x\, x^N e^{-x} = \int_0^\infty \mathrm{d}x\, e^{N\left(\ln x - \frac{x}{N}\right)}$$

Thus $\phi(x) = \ln x - \frac{x}{N}$, and

$$\phi'(x) = \frac{1}{x} - \frac{1}{N}$$

i.e., $x_{max} = N$. And

$$|\phi''(x)| = \frac{1}{x^2}$$

$$\Gamma(n+1) = \int_0^\infty \mathrm{d}x\, x^N e^{-x} = \int_0^\infty \mathrm{d}x\, e^{N\left(\ln x - \frac{x}{N}\right)} \approxeq e^{N(\ln N - 1)} \sqrt{\frac{2\pi}{N\frac{1}{N^2}}} = N^N e^{-N}\sqrt{2\pi N}$$

which is Stirling approximation. We usually want to take logarithm:

$$\ln(N!) \approxeq N\ln N - N + \frac{1}{2}\ln(2\pi N)$$

Example Back to example with up and down particles:

$$g(N,S) = \frac{N!}{N_\uparrow! N_\downarrow!}$$

where $2S = N_\uparrow - N_\downarrow$ and $N = N_\uparrow + N_\downarrow$

$$\ln g = \ln N! - \ln N_\uparrow! - \ln N_\downarrow!$$

$$\ln N! = \frac{1}{2}\ln 2\pi + (N+1)\ln N - \frac{1}{2}\ln N - N$$

Substituting

$$\ln N! = \frac{1}{2} ln\frac{2\pi}{N} + \left(N_\uparrow + \frac{1}{2} + N_\downarrow + \frac{1}{2}\right)\ln N - (N_\uparrow + N_\downarrow)$$

in addition

$$\ln N_\uparrow! = \frac{1}{2}\ln 2\pi + \left(N_\uparrow + \frac{1}{2}\right)\ln N_\uparrow - N_\uparrow$$

$$\ln N_\downarrow! = \frac{1}{2}\ln 2\pi + \left(N_\downarrow + \frac{1}{2}\right)\ln N_\downarrow - N_\downarrow$$

so

$$\ln g = \frac{1}{2} ln\frac{1}{2\pi N} - \left(N_\uparrow - \frac{1}{2}\right)\ln\frac{N_\uparrow}{N} - \left(N_\downarrow + \frac{1}{2}\right)\ln\frac{N_\downarrow}{N}$$

Now since

$$\ln\frac{N_\uparrow}{N} = \ln\left(\frac{1}{2} + \frac{2S}{2N}\right) = \ln\frac{1}{2}\left(1 + \frac{2S}{N}\right) = \ln\frac{1}{2} + \ln\left(1 + \frac{2S}{N}\right)$$

If $S \ll N$

$$\ln\frac{N_\uparrow}{N} = -\ln 2 + \frac{2S}{N} - \frac{2S^2}{N^2}$$

similarly

$$\ln\frac{N_\downarrow}{N} = -\ln 2 - \frac{2S}{N} + \frac{2S^2}{N^2}$$

Thus

$$\ln g = \frac{1}{2}\ln\frac{1}{2\pi N} - \left(\frac{1}{2}N + S - \frac{1}{2}\right)\left(-\ln 2 + \frac{2S}{N} - \frac{2S^2}{N^2}\right) - \left(\frac{1}{2}N - S + \frac{1}{2}\right)\left(-\ln 2 - \frac{2S}{N} + \frac{2S^2}{N^2}\right)$$

i.e.,

$$\ln g = \frac{1}{2} ln\frac{2}{\pi N} + N\ln 2 - \frac{2S}{N} + \mathcal{O}\left(\frac{S^3}{N^2}\right)$$

$$g(N,S) = \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} 2^N e^{-\frac{2S^2}{N}}$$

And if use energy,

$$g(N,U) = \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} 2^N e^{-\frac{2U^2}{(\mu B)^2 N}}$$

Now since number of configurations is $2N$,

$$\rho(S) = \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} e^{-\frac{2S^2}{N}}$$

Which is normal distribution with mean 0 and standard deviation $\frac{\sqrt{N}}{2}$. (This is immediate from CLT).
Lets check the standard deviation of actual S:

$$\left\langle (2S)^2 \right\rangle = \left\langle \left(\sum_i N_i\right)^2 0 \right\rangle = \left\langle \sum_{i,j} N_i N_j \right\rangle = \left\langle \sum_i N_i^2 + \underbrace{\sum_{i \neq j} N_i N_j}_{\text{0 from independence}} \right\rangle = \left\langle \sum_i N_i^2 \right\rangle = N$$

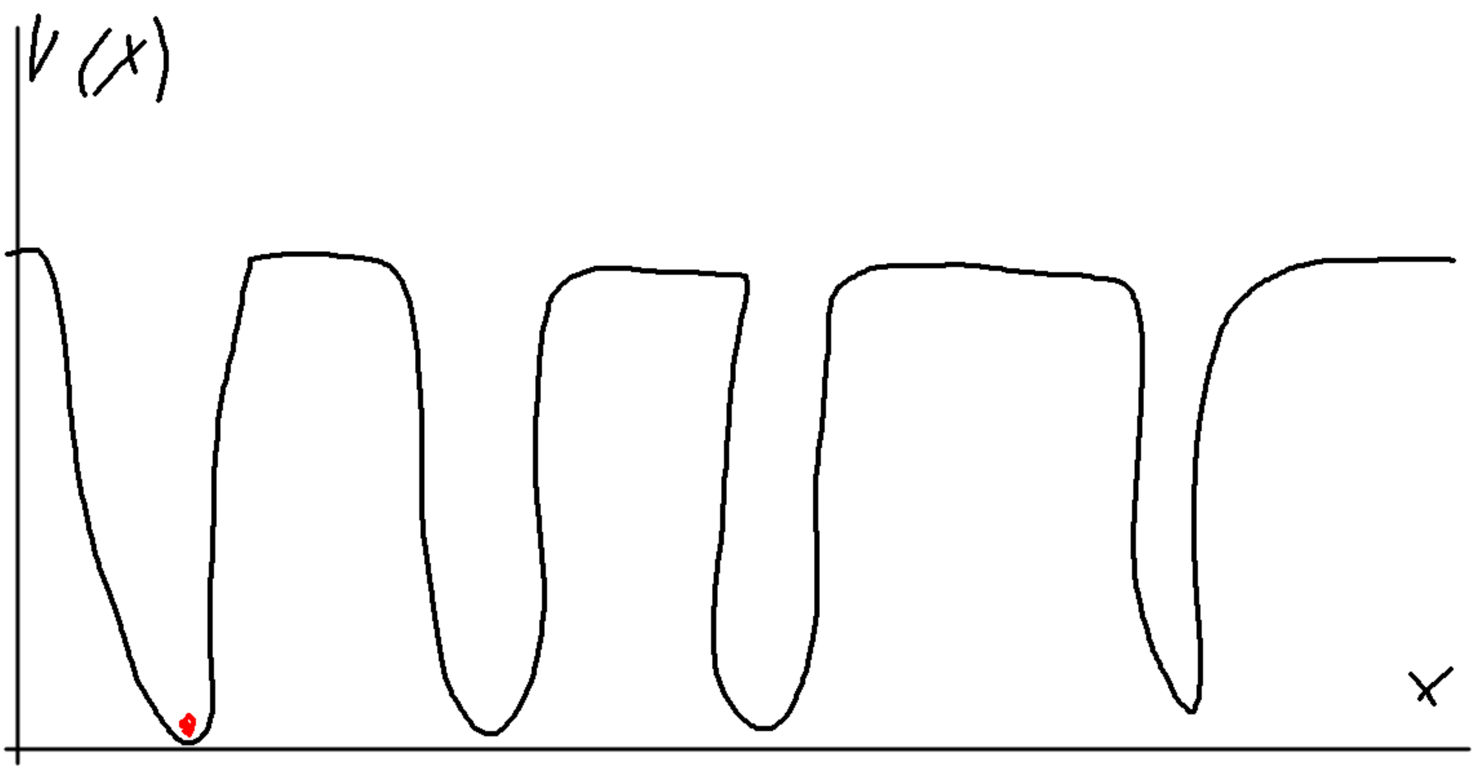
Thus variance of $2S$ is N and variance of S is $\frac{N}{4}$. Now, relative standard deviation

$$\frac{\left\langle (2S)^2 \right\rangle}{N} = \frac{1}{\sqrt{N}}$$

For that lets define new variable $X = \frac{2S}{N}$, then

$$\rho(X) = \left(\frac{N}{2\pi}\right)^{\frac{1}{2}} e^{-\frac{NX^2}{2}}$$

Ergodic hypothesis For closed system (B, E, N, V are constant) there is equal probability to acquire any of possible states. Such ctates are called **microcanonical ensemble**.
Example of exceptions:



Particle can't get out of potential well though there are other well is could possible be into.

Meaning of ergodic hypothesis Suppose we have two closed Ising systems (with magnetic moments) and we connect them: one with $N_1 = 5$ and $2S_1 = 1$ and second with $N = 10$ and $2S_2 = -2$.
Now, suppose we connected two systems to a single one.

If in each side nothing changes,

$$g_f^0 = g_i = \frac{5!}{3! \cdot 2!} \cdot \frac{10!}{6!4!}$$

If one particle changes moment such that $2S_2 = 0$:

$$g_f^1 = \frac{5!}{2! \cdot 3!} \cdot \frac{10!}{5!5!}$$

Note that $\frac{g_1^f}{g_f^0} = \frac{6}{5} > 1$.
If two particle changes moment such that $2S_2 = -2$:

$$g_f^2 = \frac{5!}{1! \cdot 4!} \cdot \frac{10!}{6!3!}$$

Note that $\frac{g_1^f}{g_f^2} = \frac{6 \cdot \cdot 4}{5 \cdot 2} > 1$.
Thus g_f^1 is most degenerated state, and the system will most of the time be on the most degenerated state. In big system, since variance of X is $\frac{1}{\sqrt{N}}$, this state will observed almost always. I.e., there is flow from second box to the first one.

Example Now lets use Gaussian approximation. Then new degeneracy is $g(N_1, S_1) \cdot g(N_2, S_2)$ and the condition is $S_1 + S_2 + S$. We also denote $N_1 + N_2 = N$. We are searching for a maximum of degeneracy under constrain.

$$g(N_1, N_2, S_1, S_2) = g_1(0)g_2(0)e^{-\frac{2S_1^2}{N_1} - \frac{2S_2^2}{N_2}}$$

Where $g_1(0)$, $g_2(0)$ are normalization constants, which doesn't affect optimization. Since $S_2 = S - S_1$:

$$g(N_1, N_2, S_1, S_2) = g_1(0)g_2(0)e^{-\frac{2S_1^2}{N_1} - \frac{2(S-S_1)^2}{N_2}}$$

We can optimize $\ln g$ instead, since, it's monotonous:

$$\ln g = C - \frac{2S_1^2}{N_1} - \frac{2(S - S_1)^2}{N_2}$$

$$\frac{\mathrm{d} \ln g}{\mathrm{d} S} = -\frac{4S_1}{N_1} + \frac{4(S - S_1)}{N_2} = 0$$

$$N_1(S - S_1) - N_2 S_1 = 0$$

$$N_1 S - N S_1 = 0$$

$$S_1 = \frac{N_1 S}{N}$$

Thus

$$S_2 = \frac{N_2 S}{N}$$

How many states are in maximal degeneracy?

$$g(N_1, N_2, S_1, S_2) = g_1(0)g_2(0)e^{-\frac{2S^2}{N}}$$

Suppose we are looking at different state

$$\begin{cases} S_1 = S_1^{max} + \delta S_2 = S_2^{max} - \delta \end{cases}$$

Then

$$g(N_1, N_2, S_1, S_2) = g_{max}(N_1, N_2, S_1, S_2) \cdot \exp\left(-\frac{4S_1^{max}\delta}{N_1} - \frac{2\delta^2}{N_1} + \frac{4S_2^{max}\delta}{N_2} - \frac{2\delta^2}{N_2}\right) = g_{max}(N_1, N_2, S_1, S_2) \cdot \exp\left(-\frac{2\delta^2}{N_1} - \frac{2\delta^2}{N_2}\right)$$

For example, if $N_1 = N_2 = 10^{22}$ and $\delta = 10^{12}$, i.e., $\frac{\delta}{N_1} = 10^{-10}$,

$$g(N_1, N_2, S_1, S_2) = g_{max}(N_1, N_2, S_1, S_2) \cdot e^{-400}$$