

Classical Statistical Mechanics

Probabilistic approach to equilibrium macroscopic physics of large numbers of degrees of freedom

Microcanonical ensemble

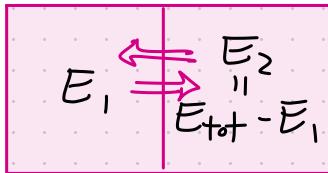


Completely isolate thermally, mechanically, or chemically from the rest of the universe

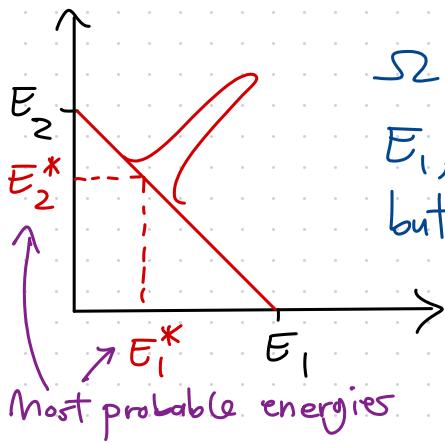
$$dN = dQ = 0, \quad dE = 0$$

$$P_{E,V,N}(\mu) = \frac{1}{\mathcal{S}(E,V,N)} \cdot \begin{cases} 1 & \text{for } H(\mu) = E \\ 0 & \text{otherwise} \end{cases}$$

Zeroth law



Two previously isolated systems are brought into thermal contact where they can exchange energy via heat. The combined system can be in any phase-space configuration that satisfies the constraint $E_{\text{tot}} = E_1 + E_2$.



$$\mathcal{S}(E_{\text{tot}}) = \int dE_1 \mathcal{S}(E_1) \mathcal{S}(E_{\text{tot}} - E_1)$$

E_1, E_2 can take any value from 0 to E_{tot} , but since \mathcal{S} is exponentially growing with N , only the most probable configuration matters in the $N \rightarrow \infty$ limit.

(We will see an instance of this phenomenon at work in the example of two-level systems below.)

$$S = k_B \ln \Omega \quad (\text{Boltzmann entropy})$$

$$\Omega(E_{\text{tot}}) = \int dE_1 \Omega(E_1) \Omega(E_{\text{tot}} - E_1)$$

$$= \int dE_1 e^{S(E_1)/k_B} e^{S(E_{\text{tot}} - E_1)/k_B}$$

[S is an extensive quantity: $S(x_1, x_2) = S(x_1) + S(x_2)$ for statistically independent degrees of freedom, so e^S is exp. in N]

$$\approx e^{S(E_1)/k_B} e^{S(E_{\text{tot}} - E_1)/k_B}$$

$$\text{Let } f(E) = \Omega(E_1) \Omega(E_{\text{tot}} - E_1)$$

$$\frac{df}{dE_1} = \frac{\partial \Omega(E_1)}{\partial E_1} \Omega(E_2) dE_1 + \Omega(E_1) \frac{\partial \Omega(E_2)}{\partial E_2} dE_2$$

$$dE = 0 \Rightarrow dE_2 = -dE_1$$

$$= \left[\frac{\partial \Omega(E_1)}{\partial E_1} \Omega(E_2) - \frac{\partial \Omega(E_2)}{\partial E_2} \Omega(E_1) \right] dE_1$$

o at the most probable configuration

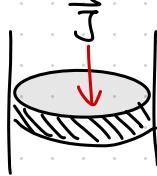
$$\Leftrightarrow \frac{1}{\Omega(E_1)} \frac{\partial \Omega(E_1)}{\partial E_1} = \frac{1}{\Omega(E_2)} \frac{\partial \Omega(E_2)}{\partial E_2} \Leftrightarrow \underbrace{\frac{\partial S_1}{\partial E_1}}_{\text{Equilibrium}} = \underbrace{\frac{\partial S_2}{\partial E_2}}$$

(Equilibrium temperature)

$$\boxed{\frac{1}{T_1} = \frac{1}{T_2}}$$

$$1/T_1 \quad 1/T_2$$

First law



Suppose that we can do work on a box of gas

$$\text{I } \delta x \quad \text{So } E_1 \quad \text{System } E_{\text{tot}} = E_1 + mgh$$

-mg
Area A

$$\text{At equilibrium, } 0 = \frac{dS}{dh} = \frac{\partial S}{\partial E_1} \frac{\partial E_1}{\partial h} + \frac{\partial S}{\partial V} \frac{\partial V}{\partial h}$$

$$\Rightarrow \frac{\partial S}{\partial V} = \frac{mg}{A} \frac{\partial S}{\partial E_1} = \boxed{\frac{P}{T}}$$

For generalized work $dW = \vec{J} \cdot \delta \vec{x}$

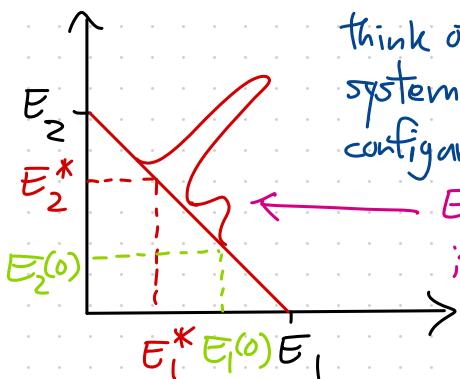
$$\begin{aligned} \Rightarrow \delta S &= \left. \frac{\partial S}{\partial E} \right|_{\vec{x}} \vec{J} \cdot \delta \vec{x} + \sum_j \left. \frac{\partial S}{\partial x_j} \right|_E \delta x_j \\ &= \underbrace{\left(\left. \frac{\partial S}{\partial E} \right|_{\vec{x}} \vec{J} + \frac{\partial S}{\partial \vec{x}} \right)}_0 \cdot \delta \vec{x} \end{aligned}$$

$$\boxed{\frac{\partial S}{\partial x_j} = - \frac{J_j}{T}}$$

Second law

$$S(E_1^*) + S(E_2^*) \geq S(E_1) + S(E_2)$$

The statement is purely probabilistic, but you can think of following the microstate of the combined system at any point in time, and the number of configurations will be less than the equilibrium one.



Even if there are more than one maxima, if $S(E_i) \leq S(E_i^*)$ then the difference in the number of configurations is $\sim e^{cN}$

The third law (the zero of entropy is when $T=0$) cannot really be derived in this classical framework.

Two-level systems (Toy example)

N atoms, each with impurity either in the ground state ($E=0$) or the excited state ($E=\varepsilon$). This discrete model is easier to work with than the ideal gas but can still demonstrate common features in the large N limit.

$$\begin{array}{l} \text{(Occupation} \\ \text{number)} \end{array} n_j = \begin{cases} 0 & \text{ground} \\ 1 & \text{excited} \end{cases}$$

$$N_e := \sum_{j=1}^N n_j = \begin{pmatrix} \text{Total number of impurities} \\ \text{in the excited state} \end{pmatrix}$$

Suppose that any microstate with energy $E=N_e\varepsilon$ is equally likely.

$$\Pr(\{n_j\}_j) = \frac{1}{S(E, N)} \delta_{E, \varepsilon N_e}$$

$$\frac{S(E, N)}{k_B} = \ln \binom{N}{N_e}$$

$$\binom{N}{N_e} = \frac{N!}{N_e!(N-N_e)!}$$

$$\begin{aligned} &\approx N \ln N - N - N_e \ln N_e + N_e - (N - N_e) \ln (N - N_e) + N - N_e \\ &= -N \left[\frac{N_e}{N} \ln \frac{N_e}{N} + \frac{N - N_e}{N} \ln \left(\frac{N - N_e}{N} \right) \right] \end{aligned}$$

$$\text{Extensive} \rightarrow = -N \left[\frac{E}{N\varepsilon} \ln \frac{E}{N\varepsilon} + \left(1 - \frac{E}{N\varepsilon}\right) \ln \left(1 - \frac{E}{N\varepsilon}\right) \right]$$

$$N_e = \frac{E}{\varepsilon}$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} \Big|_N = -Nk_B \left[\frac{1}{N\varepsilon} \ln \frac{E}{N\varepsilon} + \cancel{\frac{1}{N\varepsilon}} - \frac{1}{N\varepsilon} \ln \left(1 - \frac{E}{N\varepsilon}\right) - \cancel{\frac{1}{N\varepsilon}} \right]$$

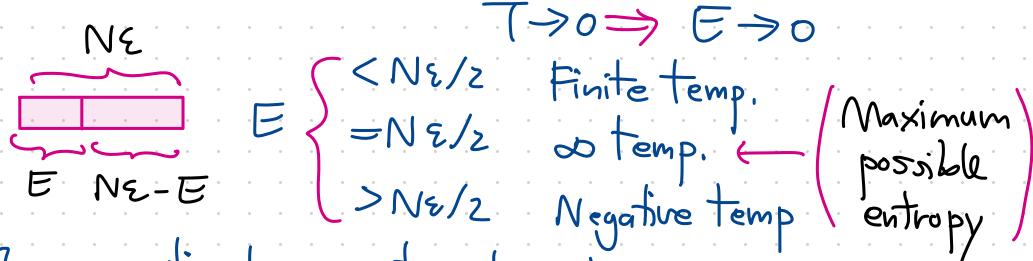
$$= -\frac{k_B}{\varepsilon} \ln \left(\frac{E}{N\varepsilon} \cdot \frac{N\varepsilon}{N\varepsilon - E} \right) = \frac{k_B}{\varepsilon} \ln \left(\frac{N\varepsilon - E}{N\varepsilon} \right)$$

$$E(T) = \frac{N\varepsilon}{e^{\varepsilon/k_B T} + 1}$$

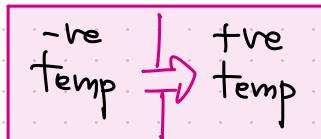
What does this tell us about the temperature?

High temp: $k_B T \gg \varepsilon$, $E(T) \approx \frac{N\varepsilon}{2}$ ε or 0 doesn't make much difference

Low temp: $k_B T \ll \varepsilon$, $E(T) \approx N\varepsilon e^{-\varepsilon/k_B T}$



In a negative-temp. system, the entropy goes up when the energy goes down because there is an upper limit to the amount of energy the system can have.



Negative temp. is hotter than any positive (even ∞) temperature.

Let us approximate \mathcal{N} for large N to see its behavior

$$\text{Define } d = N - 2N_e \Rightarrow N_e = \frac{N-d}{2}$$

$$\ln(1-x) \approx -x - \frac{x^2}{2} + \dots$$

$$\mathcal{N} = \frac{\binom{N}{N_e}}{\binom{N}{N/2}} = \frac{(N/2)!(N/2)!}{\underset{\text{Ignore}}{N_e!(N-N_e)!}} = \frac{(N/2)!(N/2)!}{\left(\frac{N-d}{2}\right)!\left(\frac{N+d}{2}\right)!} = \prod_{j=1}^{d/2} \frac{\frac{N}{2}-j+1}{\frac{N}{2}+j}$$

$$\ln \mathcal{N} = \sum_{j=1}^{d/2} \ln \left(\frac{1 - \frac{2j}{N} - \frac{2}{N}}{1 + \frac{2j}{N}} \right) \underset{\substack{\text{Near} \\ N/2}}{\approx} \sum_{j=1}^{d/2} \left(-\frac{4j}{N} \right) \approx -\frac{d^2}{2N}$$

$$\begin{aligned} \ln \frac{1-x}{1+x} &= \ln(1-x) - \ln(1+x) \\ &\approx -x - \frac{x^2}{2} - x + \frac{x^2}{2} = -2x \end{aligned}$$

$$\Rightarrow \binom{N}{N_e} \approx \binom{N}{N/2} e^{-d^2/2N} \approx \sqrt{\frac{2}{\pi N}} z^N e^{-d^2/2N}$$

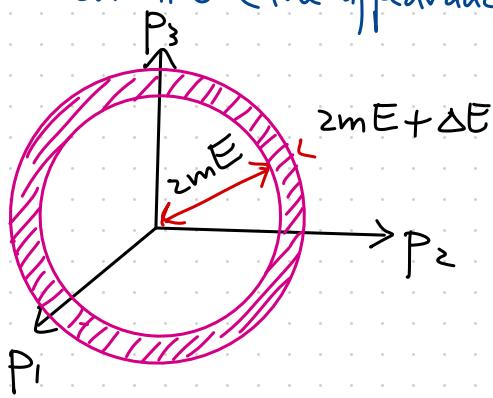
Gaussian with variance $\sim \sqrt{N} \rightarrow$ Extremely narrow when $N \rightarrow \infty$.

Microcanonical approach to the classical ideal gas

The entropy of a classical ideal (non-interacting) gas of N particles with total energy E in a box of volume V is given by

$$S = k_B N \ln \left[\frac{V}{N} \left(\frac{4\pi m E}{3\hbar^2} \right)^{3/2} \right] + \sum S_{\text{part}}$$

The Sackur-Tetrode equation cannot be completely derived classically because the zero of the entropy is set by quantum mechanics (the appearance of the Planck's constant \hbar).



The total number of microstates available to the systems come from 4 contributions:

- ① Position configuration
- ② Momentum configuration

- ③ Indistinguishability of the particles in our description
- ④ Minimum (quantum mechanically) phase-space volume.

① is easy to take care of; $S_{\text{position}} = V^N$

For ②, the microstate can be anywhere in the hyperspherical shell of radius $\sqrt{2mE}$ and thickness ΔE (which we will take to 0) in the $3N$ -dimensional Euclidean space.

Consider the Gaussian integral in n dimension

$$I_n = \int dx_1 \cdots dx_n e^{-x_1^2} \cdots e^{-x_n^2}$$

We know how to calculate this; it is just

$$I_n = \left(\int dx e^{-x^2} \right)^n = \pi^{n/2}$$

The significance of the integral is that we can transform to the (hyper)spherical coordinates by the change of variable $r^2 = \sum_{j=1}^n x_j^2$

$$I_n = \int_0^\infty dr r^{n-1} e^{-r^2} \underbrace{\int d\omega_{n-1}}_{\mu(\mathbb{S}^{n-1})} \quad \begin{pmatrix} \text{Surface area of} \\ \text{the } (n-1)\text{-dim} \\ \text{unit sphere} \end{pmatrix}$$

$$t = r^2 \Rightarrow dt = 2rdr \quad \hookrightarrow \text{Notation explained next page}$$

$$\begin{aligned} \int_0^\infty dr r^{n-1} e^{-r^2} &= \int_0^\infty \frac{dt}{2\sqrt{t}} t^{(n-1)/2} e^{-t} \\ &= \frac{1}{2} \int_0^\infty dt t^{\frac{n}{2}-1} e^{-t} = : \underbrace{\Gamma\left(\frac{n}{2}\right)}_2 \end{aligned}$$

$$\Rightarrow \int d\omega_{n-1} = \frac{2I_n}{\Gamma(n/2)} = \frac{2\pi^{n/2}}{\Gamma(n/2)}$$

$$\Gamma(n+1) = n! \quad \Leftrightarrow \quad \Gamma(n/2) = \frac{z^{(n-2)}}{z^{n/2}}, \quad n \text{ even}$$

$$\Gamma\left(n + \frac{1}{2}\right) = \sqrt{\pi} \underbrace{(2n-1)!!}_{z^n} \Leftrightarrow \Gamma(n/2) = \frac{\sqrt{2\pi}(n-2)!!}{z^{n/2}}, \quad n \text{ odd}$$

Let $S_{n-1}(r)$ denotes the sphere of radius r in n dimension
 (so it is an $(n-1)$ -dimensional surface with the constraint $r^2 = \sum_{j=1}^n x_j^2$)

For convenience, I will suppress the argument r when $r=1$
 (unit sphere).

Denote the volume of the sphere as $\mu[S_{n-1}(r)]$ and the surface area of the sphere by $\mu[\delta S_{n-1}(r)]$

$$\int d\omega_{n-1} = \mu(\delta S_{n-1})$$

Surface area
of the unit sphere

$$\mu[S_{n-1}(r)] = r^n \mu(S_{n-1})$$

$$\mu[\delta S_{n-1}(r)] = r^{n-1} \mu(\delta S_{n-1})$$

$$\begin{aligned}\mu[S_{n-1}(r)] &= \int_0^r dr' \mu[\delta S_{n-1}(r')] dr' \\ &= \mu(\delta S_{n-1}) \int_0^r dr' (r')^{n-1} = \frac{r^n}{n} \mu(\delta S_{n-1})\end{aligned}$$

That is, the volume of the sphere of radius r in n dimension is r^n/n times the total solid angle $\int d\omega_{n-1}$.

$$\int d\omega_{n-1} = \frac{2\pi^{n/2}}{\Gamma(n/2)}$$

$$\Rightarrow \mu(S_{n-1}) = \frac{\pi^{n/2}}{\frac{n}{2} \Gamma(n/2)} = \frac{\pi^{n/2}}{\Gamma(n/2 + 1)} = \frac{\pi^{n/2}}{(\frac{n}{2} + 1)!}$$

	Formula	$n=1$ (Circle)	$n=2$ (Sphere)
Solid angle	$\frac{\sum \pi^{n/2}}{\Gamma(n/2)}$	2π	πr^2
Volume	$\frac{\pi^{n/2}}{\Gamma(\frac{n}{2}+1)}$	4π	$\frac{4\pi r^3}{3}$



$$\Gamma(1) = 0! = 1$$

$$\Gamma(3/2) = \frac{\sqrt{\pi}}{2}$$

For our application, we don't exactly need the volume of the hypersphere; we only need the volume of the shell of thickness $\Delta R = \sqrt{\frac{2m}{E}} \Delta E$ by permitting the energy to be in the range $E \pm \Delta E$

$$\begin{aligned}
 \left(\text{Thickness of the shell} \right) &= \sqrt{2m(E + \Delta E)} - \sqrt{2m(E - \Delta E)} \\
 &= \sqrt{2mE} \left(\sqrt{1 + \frac{\Delta E}{E}} - \sqrt{1 - \frac{\Delta E}{E}} \right) \\
 &\approx \sqrt{2mE} \left(1 + \frac{\Delta E}{2E} - 1 + \frac{\Delta E}{2E} \right) \\
 &= \sqrt{2mE} \frac{\Delta E}{E} = \sqrt{2m/E} \Delta E
 \end{aligned}$$

$$\begin{aligned}
 (\text{Shell volume}) &= (\text{Surface area}) \times \int dE R^{3N-1} \\
 &\approx R^{3N-1} \times (\text{Shell thickness}) \\
 &= (2mE)^{\frac{3N-1}{2}} \sqrt{\frac{2m}{E}} \Delta E
 \end{aligned}$$

$$S_{\text{momentum}} = \frac{2\pi^{3N/2}}{\Gamma(3N/2)} \sqrt{\frac{2m}{E}} (2mE)^{\frac{3N-1}{2}} \Delta E$$

(3) The $N!$ correction The entropy obtained from the phase-space volume that we just derived does not give an extensive (nor an intensive) entropy expression.

$$\begin{aligned}
 \frac{S(E, V, N)}{k_B} &\approx N \ln V + \frac{3N}{2} \ln (2\pi m E) - \frac{3N}{2} \ln \frac{3N}{2} + \frac{3N}{2} \\
 &= N \left[\ln V + \ln (2\pi m E)^{3/2} - \ln \left(\frac{3N}{2} \right)^{3/2} + \ln e^{3/2} \right] \\
 &= N \ln \left[V \left(\frac{4\pi m E}{3N} \right)^{3/2} \right]
 \end{aligned}$$

Ruins the extensivity

$$\frac{S(\pi E, \pi V, \pi N)}{k_B} = \pi N \ln \left[V \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \pi N \ln \pi$$

Since we don't distinguish between different particles, any microstates that are the same after a permutation of particles should count as the same microstate, and there are $N!$ such permutations.

Dividing S_2 by $1/N!$ gives an additional factor of $-\ln N!$

$$\approx -N \ln N + N \text{ in the entropy}$$

$$\text{Let us call } \square = \left(\frac{4\pi r m \bar{E}}{3N} \right)^{3/2} \leftarrow \text{Intensive}$$

$$\begin{aligned} \frac{S(E, V, N)}{k_B} &\approx N \ln(V \square) - \ln N! \\ &\approx N \ln(V \square) - N \ln N + N \ln e \\ &= N \ln\left(\frac{V}{N} e \square\right) \end{aligned}$$

Now since only the ratio V/N appears, the quantity in the log is intensive, and the overall entropy is extensive.

A number of text books (including Kardar's) says that the $N!$ correction is natural in the framework of quantum statistical mechanics because of the indistinguishability of particles (bosons/fermions), whereas it is an additional postulate in the framework of classical statistical mechanics.

However, as E.T. Jaynes demonstrates (Jaynes' "The Gibbs paradox" 1992), whether the particles are distinguishable in our description has little to do with whether they are "truly" distinguishable; treating all particles the same simply means that we don't have an experimental procedure to separate different species of particles, and all predictions coming from such a description (e.g. work that can be extracted from the system calculated via the entropy function) will be consistent with our lack of procedure to separate the particles.

⑦ The division by h^3 . Currently our S_2 has the unit of $([\text{length}][\text{momentum}])^{3N}$. It is typical to divide S_2 by h^{3N} to make it dimensionless and simultaneously set the zero of the entropy. Many physical properties depend only on the derivative of S , so a change in an overall constant will not effect them.

$$S(E, V, N) \approx Nk_B \ln \left[\frac{V e^{5/2}}{Nh^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right]$$

Define $\rho = N/V$ and $\lambda = h / \sqrt{4\pi m E / (3N)}$

$$\Rightarrow S(E, V, N) = -Nk_B \ln(\rho \lambda^3) + \frac{5}{2} Nk_B$$

(Sackur-Tetrode)

↑
Thermal de Broglie wavelength

Thermodynamic properties from S_{ideal gas}

$$S(E, V, N) = Nk_B \ln \left[\frac{V}{N} e \left(\frac{4\pi m E}{3N} \right)^{3/2} \right]$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} \Big|_{V, N} = \frac{3}{2} \frac{Nk_B}{E} \Leftrightarrow \boxed{E = \frac{3}{2} Nk_B T} \quad (\text{Equi-partition})$$

$$\frac{P}{T} = \frac{\partial S}{\partial V} \Big|_{E, N} = \frac{Nk_B}{V} \Leftrightarrow \boxed{PV = Nk_B T} \quad (\text{Ideal gas law})$$

The chemical potential needs the $N!$ correction to be intensive:

$$\frac{\mu}{T} = \frac{\partial S}{\partial N} \Big|_{E, V} = k_B \ln \left[\frac{V}{N} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right]$$

where is e ?

Maxwell-Boltzmann distribution from S2

Marginal probability distribution of the momentum of particle 1
 (Doesn't matter which one we call particle 1; it can be any one)

Integrating out ^{The position of particle 1} $\int d\vec{q}_1$ $N-1$ other particles $\prod_{j=2}^N d^3\vec{q}_j d^3\vec{p}_j$ $\Pr(\vec{\mu})$

$$\Pr(\vec{p}_1) \propto \int d\vec{q}_1 \prod_{j=2}^N d^3\vec{q}_j d^3\vec{p}_j \Pr(\vec{\mu})$$

$$= \frac{1}{S(E, V, N)} \int d\vec{q}_1 \prod_{j=2}^N d^3\vec{q}_j d^3\vec{p}_j$$

$$= \frac{V S(E - \vec{p}_1^2/2m, V, N-1)}{S(E, V, N)}$$

$$= \frac{V^N}{(N-1)!} \frac{\pi^{3(N-1)/2}}{\Gamma[3(N-1)/2]} (2mE - \vec{p}_1^2)^{(3N-4)/2} \times \frac{N! \Gamma(3N/2)}{\sqrt{\pi} \pi^{3N/2} (2mE)^{3N/2}}$$

$$= \left(1 - \frac{\vec{p}_1^2}{2mE}\right)^{\frac{3N}{2}-2} \times \frac{N}{\pi^{3/2}} \frac{\Gamma(3N/2)}{\Gamma[3(N-1)/2]} \frac{1}{(2mE)^{3/2}}$$

$$= \left(1 - \frac{\vec{p}_1^2}{2mE}\right)^{\frac{3N}{2}-2} \times N \left(\frac{3N}{4\pi m E}\right)^{3/2}$$

$$\exp\left[-\frac{\vec{p}_1^2}{(2mE)}\right]^{\frac{3N}{2}} = \exp\left(-\frac{3N}{2} \frac{\vec{p}_1^2}{2mE}\right) = \exp\left(\frac{-\vec{p}_1^2}{2mk_B T}\right)$$

Without the \hbar^3 correction

$$S = \frac{V^N}{N!} \frac{2\pi^{3N/2}}{\Gamma(3N/2)} \sqrt{\frac{2m}{E}} (2mE)^{\frac{3N-1}{2}} \Delta E$$