Discrete Energy Levels

In this model, Boltzmann postulates in a gas of N particle, that each particle has discretely spaced value of energy kinetic ϵP. The permutation of configuration $E_k|N \equiv E_1, \dots E_N$ denote distinct configuration. State of system is then defined as set $n_k \equiv n_0, \cdot, n_P$ where n_k is the number of molecule having $k\epsilon$ energy level.

Table: system with two possible energy level $(0, \epsilon)$

State $n_{k\|P} = (n_0, n_1)$	Configuration $E_k\|N = (E_1, E_2, E_3)$
$(3, 0)$	$(0, 0, 0)$
$(2, 1)$	$(\epsilon, 0, 0), (0, \epsilon, 0), (0, 0, \epsilon)$
$(1, 2)$	$(\epsilon, \epsilon, 0), (\epsilon, 0, \epsilon), (0, \epsilon, \epsilon)$
$(0, 3)$	$(\epsilon, \epsilon, \epsilon)$

Each configuration must also obey the following restriction.

$$\sum_{k=0}^{P} = N, \quad U = \epsilon \sum_{k=0}^{P} k n_k$$

or simply

$$\sum_{k=0}^{P} = N, \quad \sum_{k=0}^{P} k n_k = L$$

The first restriction says that each configuration is in such way that the sum of each element n_k is the total number of particle N, while the second restriction rule the total energy U of the system.

To determine the total configuration of a specific configuration $n_{k|P}$, we use

$$D(N, P, n_{k|P}) = \frac{N!}{\prod_{i=0}^{P} n_i!}$$

To find the total configuration of a system, we're then summing all possible state that can be achieved by the system in question. After that, we obtain

$$D_T(N, P) = (P + 1)^N$$

For a special case when $L \leq P$, the equation above turns into

$$\mathcal{D}(N, L) = \frac{1}{L!} \frac{(N + L - 1)!}{(N - 1)!}$$

Table: State and configuration a system with $N = P = 7$, and $L \leq P$

State $n_{k\|P} = (n_0, n_1, n_2, n_3, n_4, n_5, n_6, n_7)$	Number of configuration $D(N, P, n_{k\|P})$

$(6,0,0,0,0,0,0,1)$	$\dfrac{7!}{6!0!0!0!0!0!0!1!} = 7$
$(5,1,0,0,0,0,1,0)$	$\dfrac{7!}{5!1!0!0!0!0!1!0!} = 42$
$(5,0,1,0,0,1,0,0)$	$\dfrac{7!}{5!0!1!0!0!1!0!0!} = 42$
$(5,0,0,1,1,0,0,0)$	$\dfrac{7!}{5!0!0!1!1!0!0!0!} = 42$
$(4,2,0,0,0,1,0,0)$	$\dfrac{7!}{4!2!0!0!0!1!0!0!} = 105$
$(4,1,1,0,1,0,0,0)$	$\dfrac{7!}{4!1!1!0!1!0!0!0!} = 210$
$(4,0,2,1,0,0,0,0)$	$\dfrac{7!}{4!0!2!1!0!0!0!0!} = 105$
$(4,1,0,2,0,0,0,0)$	$\dfrac{7!}{4!1!0!2!0!0!0!0!} = 105$
$(3,3,0,0,1,0,0,0)$	$\dfrac{7!}{3!3!0!0!1!0!0!0!} = 140$
$(3,2,1,1,0,0,0,0)$	$\dfrac{7!}{3!2!1!1!0!0!0!0!} = 420$
$(3,1,3,0,0,0,0,0)$	$\dfrac{7!}{3!1!3!0!0!0!0!0!} = 140$
$(2,4,0,1,0,0,0,0)$	$\dfrac{7!}{2!4!0!1!0!0!0!0!} = 105$
$(2,3,2,0,0,0,0,0)$	$\dfrac{7!}{2!3!2!0!0!0!0!0!} = 210$
$(1,5,1,0,0,0,0,0)$	$\dfrac{7!}{1!5!1!0!0!0!0!0!} = 42$
$(0,7,0,0,0,0,0,0)$	$\dfrac{7!}{0!7!0!0!0!0!0!0!} = 1$

Real™ System

Boltzmann postulates that thermal equilibrium correspond to state with the largest number of configuration. The previous example with $N = 7$ we know that the state in question is $n_{k|P} = (3,2,1,1,0,0,0,0)$. In real system with large N, it is impossible to determine the equilibrium state using method above.

By Stirling's formula, the logarithm of $D(N, P, n_{k|P})$ is expressed as

$$\ln\left[D(N,P,n_{k|P})\right] = N\ln N - N - \sum_{k=0}^{P}\left(n_k \ln n_k - n_k\right)$$

Using equation above, Boltzmann then derive the logarithm of the largest number of configuration, which of course correspond to equilibrium state. The logarithm in question expressed as

$$\ln(\mathcal{D}_{\max}) = (N+L)\ln(N+L) - L\ln(L) - N\ln(N)$$

The number of particle n_k inside configuration above is

$$n_k = N(1-x)x^k$$

where $x = L/(L+N)$. The expression n_k above maximize the D. If the average kinetic energy $u = U/N = L\epsilon/N$ is much bigger separation ϵ, n_k acn be approximated as

$$n_k = \frac{N_\epsilon}{u+\epsilon}\left(1+\frac{\epsilon}{u}\right)^{-k} \approx \frac{N\epsilon}{u}e^{-k\epsilon/u}$$

Derivation. To find the desired maximum function, we use Lagrange's multiplier method. We will maximize $D(N,P,n_{k|P})$ for $P \to \infty$

$$F(n_k) = \ln\left[D(N,P,n_{k|P})\right] - \sum_{k=0}^{P}(\alpha + k\gamma)n_k$$

with respect to n_k. Invoking Stirling's formula forln $\left[D(N,P,n_{k|P})\right]$, we have

$$F(n_k) = N\ln N - N - \sum_{k=0}^{P}(\ln n_k - 1 + \alpha + k\gamma)n_k$$

We will now begin the maximization by

$$\frac{\partial F}{\partial n_k} = 0 \implies \begin{aligned} \frac{\partial}{\partial n_k}\left(n_k \ln n_k\right) - 1 + \alpha + k\gamma &= 0 \\ \ln n_k + \alpha + k\gamma &= 0 \end{aligned}$$

Solving for n_k

$$n = e^{-\alpha - k\gamma} = \left(e^{-\alpha}\right)\left(e^{-\gamma}\right)^k$$

for convenience's sake, we use

$$n_k = Ax^k \quad \text{with} \quad A = e^{-\alpha} \wedge x = e^{-\gamma}$$

Using this result for n_k, the first restriction R_I can be written as

$$\sum_{k=0}^{P} n_k = N \implies A\sum_{k=0}^{P} x^k = N$$

the series in the equation above is a simple geometric series

$$\sum_{k=0}^{P} x^k = 1 + x + x^2 + \cdots x^P = \sum_{k=1}^{P+1} x^{k-1}$$

which can be evaluated as

$$A\frac{1-x^{P+1}}{1-x}=N$$

Hence

$$A=N\frac{1-x}{1-x^{P+1}}$$

Whereas the second restriction reads

$$\sum_{k=0}^{P}kn_k=L \implies A\sum_{k=0}^{P}kx^k=L$$

This series is more complicated than before, however it still might be evaluated into

$$L=Ax\frac{\left\{\left[P\left(x-1\right)-1\right]x^P+1\right\}}{(x-1)^2}$$

where we have invoked WolframAlpha to evaluate the said series. For a real™ system, we have $P\to\infty$, therefore those two expression turn into

$$A=\lim_{P\to\infty}N\frac{1-x}{1-\exp(-\gamma P-\gamma)}=N(1-x)$$

and

$$L=\frac{Ax}{(x-1)^2}\lim_{P\to\infty}\left[(P(x-1)e^{-\gamma P}+1)+1\right]=-\frac{Nx(x-1)}{(x-1)^2}=\frac{Nx}{1-x}$$

Rearranging the equation above

$$x=\frac{L}{L+N}$$

Since have found the expression for A, L, and x, we can then write the complete expression for n_k

$$n_k=\frac{N(1-x)}{1-x^{P+1}}x^k$$

applying the condition for real system, we have n_k which maximize the configuration

$$n_k=N(1-x)x^k\lim_{P\to\infty}\frac{1}{1-\exp\left[-\gamma(P+1)\right]}=N(1-x)x^k$$

Substituting n_k we just obtained inside the expression of $\ln D$, we get

$$\ln(\mathcal{D}_{\max})=-N\left(\ln(1-x)+\frac{x}{1-x}\ln(x)\right)$$

expressing the equation above in terms of L and N to get

$$\ln(\mathcal{D}_{\max})=(N+L)\ln(N+L)-L\ln(L)-N\ln(N)$$

Result

We shall now discuss the result of Boltzmann derivation. The case in this discussion will be the same as previously, which is $N = P = 7, L \leq P$. Here we will compare those three result:

1. **Small system**. By this consideration, we know the equilibrium state represented by the following state

$$n_{k|P} = (3, 2, 1, 1, 0, 0, 0, 0)$$

   which has 420 number of configuration.

2. **Large system**. Tools we used in this consideration are Stirling's approximation and Lagrange multiplier. We obtain the formula for number of particle n_k with $k\epsilon$ energy

$$n_k = \frac{N(1-x)}{1-x^{P+1}} x^k$$

   where x is obtained by solving the following equation

$$(NP - L)x^{P+2} - (NP + N - L)x^{P+1} + (L + N) = 0.$$

   Boltzmann solved the equation numerically and obtained $x = 0.5078125$.

3. **Large system with large P approximation.** The equation for n_k in this consideration is written as

$$n_k = N(1-x)x^k$$

Table: The result of those three considerations. Quite accurate except few numbers.

k	n_k for small system	n_k for large system	Same but with large P approximation
0	3	3.4535	3.5
1	2	1.7574	1.75
2	1	0.8943	0.875
3	1	0.4551	0.4375
4	0	0.2316	0.2187
5	0	0.1178	0.10937
6	0	0.0599	0.05468
7	0	0.0304	0.02734