

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 $n_k \equiv n_0, \dots, n_P$ 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.

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

or simply

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

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

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

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 $D(N, P, n_{k P})$
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(6, 0, 0, 0, 0, 0, 0, 1)	$\frac{7!}{6!0!0!0!0!0!1!} = 7$
(5, 1, 0, 0, 0, 0, 1, 0)	$\frac{7!}{5!1!0!0!0!0!1!0!} = 42$
(5, 0, 1, 0, 0, 1, 0, 0)	$\frac{7!}{5!0!1!0!0!1!0!0!} = 42$
(5, 0, 0, 1, 1, 0, 0, 0)	$\frac{7!}{5!0!0!1!1!0!0!0!} = 42$
(4, 2, 0, 0, 0, 1, 0, 0)	$\frac{7!}{4!2!0!0!0!1!0!0!} = 105$
(4, 1, 1, 0, 1, 0, 0, 0)	$\frac{7!}{4!1!1!0!1!0!0!0!} = 210$
(4, 0, 2, 1, 0, 0, 0, 0)	$\frac{7!}{4!0!2!1!0!0!0!0!} = 105$
(4, 1, 0, 2, 0, 0, 0, 0)	$\frac{7!}{4!1!0!2!0!0!0!0!} = 105$
(3, 3, 0, 0, 1, 0, 0, 0)	$\frac{7!}{3!3!0!0!1!0!0!0!} = 140$
(3, 2, 1, 1, 0, 0, 0, 0)	$\frac{7!}{3!2!1!1!0!0!0!0!} = 420$
(3, 1, 3, 0, 0, 0, 0, 0)	$\frac{7!}{3!1!3!0!0!0!0!0!} = 140$
(2, 4, 0, 1, 0, 0, 0, 0)	$\frac{7!}{2!4!0!1!0!0!0!0!} = 105$
(2, 3, 2, 0, 0, 0, 0, 0)	$\frac{7!}{2!3!2!0!0!0!0!0!} = 210$
(1, 5, 1, 0, 0, 0, 0, 0)	$\frac{7!}{1!5!1!0!0!0!0!0!} = 42$
(0, 7, 0, 0, 0, 0, 0, 0)	$\frac{7!}{0!7!0!0!0!0!0!0!} = 1$

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

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

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

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

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 can 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 $P \rightarrow \infty$

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

with respect to n_k . Invoking Stirling's formula for $\ln [D(N, P, n_{k|P})]$, 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

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

Solving for n_k

$$n_k = e^{-\alpha - k\gamma} = (e^{-\alpha}) (e^{-\gamma})^k$$

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

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

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

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

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

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

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

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

and

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

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

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

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

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

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

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

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

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

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