Ludwig Boltzmann

Figure: Ludwig Boltzmann, by P. L. Dutton

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 $E_k|N \equiv E_1, \ldots E_N$ 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.

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

or simply

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

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

$$D(N, P, n_{k|P}) = N! \left(\prod_{i=0}^{P} n_i! \right)^{-1}$$

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

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

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

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

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

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

Proof. 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

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

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 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

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

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

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

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

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

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

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

   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

Continuous Energy Distribution

Assume continuous energy E within interval $(0, \infty)$, with a space of ϵ. The function $f(E)$ denote the number of atoms per unit energy. The density function $f(E)$ for continuous energy levels at equilibrium is given by

$$f(E) = \frac{N}{u} e^{-E/u}$$

Permutability measure is defined as

$$\Omega = -\int_0^\infty f(E) \ln\left[f(E)\right]\, dE$$

which, on using the given expression for density function evaluates into

$$\Omega = N(1 + \ln u - \ln N)$$

Derivation. Let n_k be the number of atoms whose energy lies between $(k\epsilon, k\epsilon + \epsilon)$. For any positive integer k,

$$n_k = \epsilon f(k\epsilon)$$

By taking the limit of $\epsilon \to 0$, n_k now denote the number of atoms whose energy lies between $(E, E + dE)$

$$\lim_{\epsilon \to 0} n_k = f(E) \lim_{\epsilon \to 0} \epsilon$$

As it the case with discrete model, we have the following restriction

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

By using the expression for n_k when $\epsilon \to 0$ these restrictions now read as

$$\int_0^\infty f(E)\, dE = N, \quad \int_0^\infty E f(E)\, dE = Nu$$

Now we consider the expression for number of configuration in the limit $D \to \mathcal{P}$. The expression for the logarithm of D written as

$$\ln D = N \ln N - N - \sum_{k=0}^{\infty} (n_k \ln n_k - n_k)$$

By taking the limit $\epsilon \to 0$, we have

$$\begin{aligned}
\ln \mathcal{P} &= N \ln N - N - \int_0^\infty \left[f(E) \ln(n_k) - f(E) \right] \, dE \\
&= N \ln N - N - \int_0^\infty f(E) \ln[f(E)] \, dE - \lim_{\epsilon \to 0} \int_0^\infty f(E) \ln(\epsilon) \, dE \\
&\quad + \int_0^\infty f(E) \, dE \\
\ln \mathcal{P} &= N \ln N - \int_0^\infty f(E) \ln[f(E)] \, dE - N \lim_{\epsilon \to 0} \ln(\epsilon)
\end{aligned}$$

Recall that equilibrium state correspond to the largest number of configuration. Although the equation above, due to the last term, diverges; it can be ignored since maximization does not concern constant. In essence, we what to maximize the logarithm of $\mathcal{P}$ by varying the expression for $f(E)$. Therefore, we maximize the quantity of

$$\Omega \equiv - \int_0^\infty f(E) \ln[f(E)] \, dE$$

which is defined as permutability measure, with N and Nu constraint. By the Lagrange multiplier method, we have the following auxiliary function

$$F(f) = \int_0^\infty \left[f \ln(f) + \lambda_1 f + \lambda_2 E f \right] dE$$

Then, we set its derivative to zero

$$\frac{dF}{df} = \int_0^\infty \left[\ln f + 1 \lambda_1 + \lambda_2 E \right] dE = 0$$

One possible way for an integral to be zero is that the integrand is zero, hence we have

$$\ln f + 1 + \lambda_1 + \lambda_2 E = 0$$

which implies

$$\begin{aligned}
f(E) &= \exp(-1 - \lambda_1 - \lambda_2 E) \\
f(E) &= C e^{-\lambda_2 E}
\end{aligned}$$

On Using this expression, N constraint now may be evaluated as

$$N = \int_0^\infty C e^{-\lambda_2 E} \, dE = \left. \frac{C e^{\lambda_2 E}}{\lambda_2} \right|_\infty^0 = \frac{C}{\lambda_2}$$

As for Nu constraint

$$\begin{aligned}
Nu &= \int_0^\infty E C e^{-\lambda_2 E} \, dE = C e^{-\lambda_2 E} \left(\frac{E}{-\lambda_2} - \frac{1}{\lambda_2^2} \right) \Bigg|_0^\infty \\
&= \left. \frac{C E e^{\lambda_2 E}}{\lambda_2} \right|_\infty^0 + \left. \frac{C e^{-\lambda_2 E}}{\lambda_2^2} \right|_\infty^0 = \frac{C}{\lambda_2^2} = \frac{N}{\lambda_2}
\end{aligned}$$

We have

$$C = \frac{N}{u} \quad \wedge \quad \lambda_2 = \frac{1}{u}$$

Hence

$$f(E) = Ce^{-\lambda_2 E} = \frac{N}{u} e^{-E/u} \quad \blacksquare$$

Now we evaluate the expression permutability measure

$$\begin{aligned}
\Omega &= -\int_0^\infty \frac{N}{u} e^{-E/u} \ln\left[\frac{N}{u} e^{-E/u}\right] dE \\
&= -\int_0^\infty \frac{N}{u} e^{-E/u} \left[\ln\left(\frac{N}{u}\right) - \frac{E}{u}\right] dE \\
&= Ne^{E/u} \ln\left(\frac{N}{u}\right)\bigg|_0^\infty + \frac{N}{u^2}\left(-Eu - u^2\right) e^{E/u}\bigg|_0^\infty \\
\Omega &= -N\ln\left(\frac{N}{u}\right) + N = N(1 + \ln U - \ln N) \quad \blacksquare
\end{aligned}$$

Velocity Distribution

Consider continuous varying value of velocity $\mathbf{v}$ within $(-\infty, \infty)$. The number of particle per unit interval is given by

$$f(\mathbf{v}) = N\left(\frac{3m}{4\pi u}\right)^{3/2} \exp\left(-\frac{3mv^2}{4u}\right)$$

Using the relation for gas ideal $u = 3k_B T/2$, one can obtain the same distribution function that Maxwell derived

$$f(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right)$$

Derivation. Let $n_\mathbf{k}$ be the number of particle whose velocity lies within $(\boldsymbol{\epsilon}\mathbf{v}, \boldsymbol{\epsilon}\mathbf{v} + \boldsymbol{\epsilon})$, so

$$n_\mathbf{k} = \boldsymbol{\epsilon} f(\mathbf{kv})$$

and as $\boldsymbol{\epsilon} \to 0$

$$n_\mathbf{k} = f(\mathbf{v}) \lim_{\boldsymbol{\epsilon}\to 0} \boldsymbol{\epsilon} = f(\mathbf{v})\, d^3v$$

As before, we want to find the equilibrium distribution function, $f(\mathbf{v})$ in this case, by maximizing the said distribution function, constrained by N and Nu function. The N constraint simply evaluate into

$$N = \int_{\mathbb{R}^3} f(\mathbf{v})\, d^3v$$

Recall that Nu stands for total energy. In the present case, we involve velocity into our consideration, hence the energy in question is the kinetic energy, which is evaluated by

$$Nu = \frac{m}{2}\langle v^2\rangle = \frac{m}{2}\int_{\mathbb{R}^3} v^2 f(\mathbf{v})\, d^3v$$

Since $f(\mathbf{v})$ is a function of v alone, we can make the change of variable $d^3v = v^2 \sin\theta\, dv\,; d\theta\, d\phi$. Thus, our constraint equations read

$$4\pi\int_0^\infty v^2 f(\mathbf{v})\, dv = N, \quad 4\pi\int_0^\infty v^4 f(\mathbf{v})\, dv = Nu$$

We then consider the number of configuration $\mathcal{P}$, which is given by

$$\mathcal{P} = N! \left(\prod_{\mathbf{k}=-\infty}^{\infty} n_{\mathbf{k}}! \right)$$

Taking the logarithm and applying Stirling's approximation,

$$\ln \mathcal{P} = N \ln N - N - \sum_{\mathbf{k}=-\infty}^{\infty} (n_{\mathbf{k}} \ln n_{\mathbf{k}} - n_{\mathbf{k}})$$

Taking the limit $\boldsymbol{\epsilon} \to 0$

$$\ln \mathcal{P} = N \ln N - N - \int_{\mathbb{R}^3} f(\mathbf{v}) \ln[f(\mathbf{v})] \; d^3v - \lim_{\boldsymbol{\epsilon} \to 0} \int_{\mathbb{R}^3} f(\mathbf{v}) \ln(\boldsymbol{\epsilon}) \; d^3v$$
$$+ \int_{\mathbb{R}^3} f(\mathbf{v}) \; d^3v$$
$$\ln \mathcal{P} = N \ln N - \int_{\mathbb{R}^3} f(\mathbf{v}) \ln[f(\mathbf{v})] \; d^3v - N \lim_{\boldsymbol{\epsilon} \to 0} \ln(\boldsymbol{\epsilon})$$

To maximize the logarithm of $\mathcal{P}$, we defined permutability measure by

$$\Omega = -\int_{\mathbb{R}^3} f(\mathbf{v}) \ln[f(\mathbf{v})] \; d^3v$$

and maximize it with the N and Nu constraint. We use the first form of those constraints, since they look simpler, and use the second form to evaluate the resulting maximized function, since we can't evaluate it using the first form. Anyway, the auxiliary function reads as

$$F(f) = \int_{\mathbb{R}^3} \left[f \ln(f) + \lambda_1 f + \lambda_2 \frac{m}{2} v^2 f \right] \; d^3v$$

As for its derivative,

$$\frac{dF}{df} = \int_{\mathbb{R}^3} \left[\ln(f) + 1 + \lambda_1 + \lambda_2 \frac{m}{2} v^2 \right] \; d^3v = 0$$

which implies

$$\ln(f) + 1 + \lambda_1 + \lambda_2 \frac{m}{2} v^2 = 0$$

Thus

$$f(\mathbf{v}) = \exp\left(-1 - \lambda_1 - \lambda_2 \frac{m}{2} v^2 \right) = C \exp\left(-\frac{\lambda_2 m}{2} v^2 \right)$$

We now use this to evaluate both constraints and determine the value for each constant. For the N constraint

$$N = 4\pi \int_0^\infty v^2 C \exp\left(-\frac{\lambda_2 m}{2} v^2 \right) \; dv = \frac{4\pi C}{2} \left(\frac{2}{m\lambda_2} \right)^{3/2} \frac{\sqrt{\pi}}{2}$$
$$= C \left(\frac{2\pi}{m\lambda_2} \right)^{3/2}$$

Then the Nu constraint

$$Nu = 4\pi \int_0^\infty v^4 C \exp\left(-\frac{\lambda_2 m}{2} v^2 \right) \; dv = \frac{4\pi C m}{4} \left(\frac{2}{m\lambda_2} \right)^{5/2} \frac{3\sqrt{\pi}}{4}$$
$$= \frac{3}{4} C m \left(\frac{2\pi^{3/5}}{m\lambda_2} \right)^{5/2}$$

Solving both for N and equating them

$$
\begin{aligned}
C\left(\frac{2\pi}{m\lambda_2}\right)^{3/2} &= \frac{3}{4}Cm\left(\frac{2\pi^{3/5}}{m\lambda_2}\right)^{5/2} \\
\frac{4u}{3} &= \frac{2m}{m\lambda_2} \\
\lambda_2 &= \frac{3}{2u}
\end{aligned}
$$

On using this to N constraint

$$
N = C\left(\frac{2\pi}{m}\frac{2u}{3}\right)^{3/2} \implies C = N\left(\frac{3m}{4\pi u}\right)^{3/2}
$$

Hence

$$
f(\mathbf{v}) = C\exp\left(-\frac{\lambda_2 m}{2}v^2\right) = N\left(\frac{3m}{4\pi u}\right)^{3/2}\exp\left(-\frac{3m}{4u}v^2\right) \quad \blacksquare
$$