

Classical Statistics of Maxwell-Boltzmann

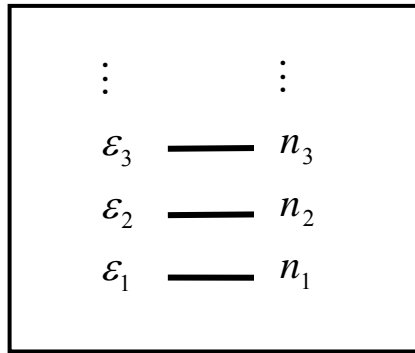
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Classical Statistics of Maxwell-Boltzmann

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Classical Statistics of Maxwell-Boltzmann

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($\epsilon_1 < \epsilon_2 < \epsilon_3, \dots$) ($\epsilon_1, \epsilon_2, \epsilon_3, \dots$) -1
 (n_1, n_2, n_3, \dots) -2

:

N -I

$$N = \sum_i n_i, \tag{1}$$

U -II

$$U = \sum_i n_i \epsilon_i \tag{2}$$

(C)

j

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$$\tilde{\omega} = \omega \{n_i\} = \frac{N!}{\prod_{i=1}^j n_i!} \tag{3}$$

\tilde{n}_i

Classical Statistics of Maxwell-Boltzmann

$$\tilde{\omega} \quad \delta \tilde{\omega} = 0 \quad \text{"}\tilde{\omega}\text{"} \quad \{n_i\} \quad \tilde{n}_i \rightarrow \tilde{n}_i + \delta n_i$$

(2) (1)

$$\delta N = \sum_i \delta n_i = 0 \tag{4}$$

$$\delta U = \sum_i \epsilon_i \delta n_i = 0 \tag{5}$$

$$\delta \ln \tilde{\omega} = 0 \tag{6}$$

$$\tilde{\omega} \quad \delta \tilde{\omega} = 0 \quad \text{"Monotonic function" ()} \quad \ln \tilde{\omega}$$

$$\ln(z!) = z \ln(z) - z \tag{3}$$

$$\ln(\tilde{\omega}) = N \ln N - \sum_i n_i \ln n_i \tag{7}$$

$$\delta \ln(\tilde{\omega}) = - \sum_i \ln n_i \delta n_i \tag{8}$$

$$\ln(\tilde{\omega}) = \ln\left(\frac{N!}{\prod_{i=1}^n n_i!}\right) = \ln(N!) - \ln\left(\prod_{i=1}^n n_i!\right)$$

$$= \ln(N!) - \ln[n_1! \times n_2! \times \dots \times n_n!]$$

$$= \ln(N!) - [\ln(n_1!) + \ln(n_2!) + \dots] = \ln(N!) - \sum_i \ln(n_i!)$$

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$$\begin{aligned}
 \ln(\tilde{\omega}) &= N \ln N - N - \sum_i (n_i \ln n_i - n_i) \\
 &= N \ln N - N - \sum_i n_i \ln n_i - \underbrace{\sum_i n_i}_N \\
 &= N \ln N - \sum_i n_i \ln n_i \tag{7a}
 \end{aligned}$$

$$\begin{aligned}
 \delta \ln(\tilde{\omega}) &= \delta(N \ln N) - \sum_i \ln n_i \delta n_i - \sum_i n_i \underbrace{\delta(\ln n_i)}_{\frac{1}{n_i} \delta n_i} \\
 &= 0 - \sum_i \ln n_i \delta n_i - \underbrace{\sum_i \delta n_i}_{=0} \\
 &= -\sum_i \ln n_i \delta n_i \tag{8a}
 \end{aligned}$$

$$\ln(\tilde{\omega}) \tag{8a}$$

δn_i

(2) (1)

:

(3)

()

-i

(Non - Degenerate levels)

$$\begin{aligned}
 (2) \quad \alpha \quad (1) \quad n_i \quad (B) \quad (8) \quad -\beta
 \end{aligned}$$

Classical Statistics of Maxwell-Boltzmann

$$\delta \left[\ln(\tilde{\omega}) + \alpha \sum_i n_i - \beta \sum_i \varepsilon_i n_i \right] = 0 \tag{11}$$

$$\sum_i [-\ln n_i + \alpha - \beta \varepsilon_i] \delta n_i = 0 \tag{11}$$

$$\sum_i [-\ln n_i + \alpha - \beta \varepsilon_i] \delta n_i = 0$$

$$\boxed{n_i = e^{\alpha - \beta \varepsilon_i}} \tag{12}$$

$$e^{-\beta \varepsilon_i} \tag{12}$$

(Degenerate States) -ii

g_i "i" n_i

$$\prod_{i=1}^j g_i^{n_i} \cdot g_i^{n_i}$$

$$\tilde{\omega}\{n_i\} = N! \prod_{i=1}^j \frac{g_i^{n_i}}{n_i!} \tag{13}$$

$$N!$$

$$\tilde{\omega}\{n_i\} = \frac{N!}{N!} \prod_{i=1}^j \frac{g_i^{n_i}}{n_i!} = \prod_{i=1}^j \frac{g_i^{n_i}}{n_i!} \tag{13a}$$

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$$\ln(\tilde{\omega}) = \sum_i n_i \left(\ln \frac{g_i}{n_i} + 1 \right) \tag{13}$$

$$\delta \ln(\tilde{\omega}) = \sum_i \ln \frac{g_i}{n_i} \delta n_i \tag{14}$$

$$n_i = g_i e^{\alpha - \beta \epsilon_i} \tag{15}$$

$$N = \sum_i n_i = \sum_i g_i e^{\alpha - \beta \epsilon_i} = e^{\alpha} \sum_i g_i e^{-\beta \epsilon_i} \tag{15}$$

Classical Statistics of Maxwell-Boltzmann

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$$\begin{aligned}\bar{E} &= \frac{1}{N} \sum_i n_i \varepsilon_i = \frac{1}{Z_{\text{sp}}} \sum_i \varepsilon_i g_i e^{-\beta \varepsilon_i} \\ &= -\frac{1}{Z_{\text{sp}}} \frac{\partial}{\partial \beta} \sum_i g_i e^{-\beta \varepsilon_i} = -\frac{1}{Z_{\text{sp}}} \frac{\partial Z_{\text{sp}}}{\partial \beta}\end{aligned}$$

$$\Rightarrow \boxed{\bar{E} = -\frac{\partial}{\partial \beta} [\ln(Z_{\text{sp}})]} \quad (20)$$

:

$$\Rightarrow \boxed{U = N \bar{E} = -N \frac{\partial}{\partial \beta} [\ln(Z_{\text{sp}})]} \quad (21)$$

:

-1

$$\overline{E^2} = \frac{1}{Z_{\text{sp}}} \frac{\partial^2 Z_{\text{sp}}}{\partial \beta^2}$$

-2

$$\sigma^2 = \overline{E^2} - (\bar{E})^2 = \frac{\partial^2}{\partial \beta^2} \ln Z_{\text{sp}}$$

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Classical Statistics of Maxwell-Boltzmann

$$\begin{aligned}
\bar{P} &= -\left(\frac{\partial \bar{E}}{\partial V}\right)_{S,N} \\
&= \frac{1}{Z_{\text{sp}}} \sum_i g_i e^{-\beta \varepsilon_i} \left(-\frac{\partial \varepsilon_i}{\partial V}\right)_{T,N} \\
&= \frac{1}{\beta Z_{\text{sp}}} \left(\frac{\partial Z_{\text{sp}}}{\partial V}\right) = \frac{1}{\beta} \left(\frac{\partial \ln(Z_{\text{sp}})}{\partial V}\right)_{T,N} \\
\Rightarrow \quad &\boxed{\bar{P} = \frac{1}{\beta} \left(\frac{\partial \ln(Z_{\text{sp}})}{\partial V}\right)_{T,N}} \quad (22)
\end{aligned}$$

$$\begin{array}{ccc}
& S & -V \\
& : & \\
& & (16)
\end{array}$$

$$\begin{array}{ccc}
\ln(n_i) = \ln N - \ln Z_{\text{sp}} - \beta \varepsilon_i & & \\
& : & \\
& & (7)
\end{array}$$

$$\begin{array}{ccc}
S = k_B \ln(\tilde{\omega}) = k_B \left(N \ln N - \sum_i n_i \ln n_i \right) & & \\
& : &
\end{array}$$

$$\begin{aligned}
S &= k_B \left(N \ln N - \sum_i n_i \underbrace{\ln n_i}_{\ln N - \ln Z_{\text{sp}} - \beta \varepsilon_i} \right) \\
&= k_B \left(N \ln N - \ln N \underbrace{\sum_i n_i}_N + \ln Z_{\text{sp}} \underbrace{\sum_i n_i}_N + \beta \underbrace{\sum_i n_i \varepsilon_i}_U \right) \\
\Rightarrow \quad &\boxed{S = k_B N \ln Z_{\text{sp}} + k_B \beta U} \quad (23)
\end{aligned}$$

Classical Statistics of Maxwell-Boltzmann

.(2) (1)

$$\beta \quad -vi$$

$$: \quad \beta$$

$$: \quad TdS = dU + PdV \quad -1$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V \quad (a)$$

: (23) -2

$$\left(\frac{\partial S}{\partial U} \right)_V = k_B N \underbrace{\frac{d \ln Z_{sp}}{d \beta}}_{-\frac{U}{N}} \left(\frac{\partial \beta}{\partial U} \right)_V + k_B \beta + k_B U \left(\frac{\partial \beta}{\partial U} \right)_V$$

$$= k_B \beta \quad (b)$$

$$(a) \quad .(21) \quad \frac{d \ln Z_{sp}}{d \beta} = -\frac{U}{N}$$

$$\beta = \frac{1}{k_B T} : \quad (b)$$

$$\beta = \frac{1}{k_B T} :$$

$\frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2},$ $\frac{\partial}{\partial \beta} = \frac{\partial T}{\partial \beta} \frac{\partial}{\partial T} = -k_B T^2 \frac{\partial}{\partial T}$ $\frac{\partial}{\partial \beta} [\ln(Z_{sp})] = -k_B T^2 \frac{\partial}{\partial T} [\ln(Z_{sp})]$

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$$F \qquad \qquad \qquad -vii$$

$$\begin{aligned}
 F &= U - TS \\
 &= U - T (k_B N \ln Z_{sp} + k_B \beta U) \\
 &= U - Nk_B T \ln Z_{sp} - \underbrace{\beta k_B T}_{1/\beta} U \\
 \Rightarrow \quad &\boxed{F = -Nk_B T \ln Z_{sp}} \qquad (24)
 \end{aligned}$$

: - III

$$\begin{array}{rcc}
 & \varepsilon & -1 \\
 .T & & \\
 & N & - \\
 & T \rightarrow \infty \quad T \rightarrow 0 & -
 \end{array}$$

$$\begin{array}{rcc}
 n_2 & n_1 & - \\
 & & : N
 \end{array}$$

$$N = n_1 + n_2$$

.ε

$$n_1 = cNe^0 = cN,$$

$$n_2 = cNe^{-\beta\varepsilon}$$

$$: \qquad N = n_1 + n_2$$

$$c = \frac{1}{1 + e^{-\varepsilon/k_B T}}$$

:

Classical Statistics of Maxwell-Boltzmann

$$E_{total} = 0 \times E_1 + \varepsilon \times N_2 = \varepsilon \times N_2$$

:

$$C = \frac{dE_{total}}{dT} = \varepsilon \times \frac{dN_2}{dT} = \frac{N \varepsilon^2}{k_B T^2} \frac{e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})^2}$$

$$: \quad 1 + e^{-\varepsilon/k_B T} \approx 1 \quad T \rightarrow 0 \quad -$$

$$C = \frac{N \varepsilon^2}{k_B T^2} e^{-\varepsilon/k_B T}$$

$$: \quad e^{-\varepsilon/k_B T} \approx 1 \quad T \rightarrow \infty \quad -$$

$$C = \frac{N \varepsilon^2}{4k_B T^2}$$

$$(\varepsilon_1 = 0, \varepsilon_2 = \varepsilon, \varepsilon_3 = 2\varepsilon) \quad \quad \quad \mathbf{4000} \quad \quad \mathbf{-2}$$

$$. g_i = g \quad \quad \quad \varepsilon$$

$$. 2300\varepsilon$$

$$n_2$$

$$. n_3$$

$$n_1$$

:

$$n_i = g_i e^{-\alpha - \beta \varepsilon_i}$$

$$\Rightarrow n_1 = g e^{-\alpha}, \quad n_2 = g e^{-\alpha - \beta \varepsilon}, \quad n_3 = g e^{-\alpha - 2\beta \varepsilon}$$

$$. n_3 = n_1 x^2 \quad n_2 = n_1 x \quad x = e^{-\beta \varepsilon}$$

:

$$n_1 + n_2 + n_3 = n_1 + n_1 x + n_1 x^2 = 4000,$$

$$\Rightarrow \boxed{n_1(1 + x + x^2) = 4000} \quad \quad \quad \mathbf{(a)}$$

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$$\begin{aligned}
 & : \\
 n_1 \times 0 + n_2 \times \varepsilon + n_3 \times 2\varepsilon &= n_1 \times 0 + n_1 x \times \varepsilon + n_1 x^2 \times 2\varepsilon \\
 &= 2300\varepsilon, \\
 \Rightarrow \boxed{n_1(x + 2x^2) = 2300} & \quad (b) \\
 & : \quad (b) \quad (a) \quad n_1
 \end{aligned}$$

$$\begin{aligned}
 57x^2 + 17x - 23 &= 0 \\
 .x = -0.802 \quad x &= 0.5034
 \end{aligned}$$

$$\begin{aligned}
 n_1 &= \frac{2300}{0.5034 + 2(0.5034)^2} \approx 2277, \\
 n_2 &= n_1 x = 1146, \\
 n_3 &= n_1 x^2 = 577
 \end{aligned}$$

$$\omega_1 = \tilde{\omega} = \frac{g^{4000}}{(2277!) \times (1146!) \times (577!)}$$

n_1

n_2

$: n_3$

$$\omega_2 = \frac{g^{4000}}{(2278!) \times (1144!) \times (578!)}$$

$\omega_2 \omega_1$

$$\frac{\omega_2}{\omega_1} = 0.9966$$

ω_1

Classical Statistics of Maxwell-Boltzmann

-3

$0, 1\varepsilon, 2\varepsilon$

$.V$

: $g_1 = 2, g_2 = 1, g_3 = 1,$

-
-
-

(a,b)

: $g_1 = 2$

Energy(الطاقة)	Microstates (الحالات المجهرية)							
	1		2		3		4	
2ε	0		0		0		0	
ε	0		0		0		0	
0	a	b	a	b	a	b	a	b
$E_0 =$	0		0		0		0	

Energy(الطاقة)	Microstates (الحالات المجهرية)							
	5		6		7		8	
2ε	0		0		0		0	
ε	b		a		b		a	
0	a	b	a	b	a	b	a	b
$E_1 =$	ε		ε		ε		ε	

Energy(الطاقة)	Microstates (الحالات المجهرية)									
	9		10		11		12		13	
2ε	b		a		b		a		0	
ε	0		0		0		0		ab	
0	a	b	a	b	a	b	a	b	a	b
$E_2 =$	2ε		2ε		2ε		2ε		2ε	

Classical Statistics of Maxwell-Boltzmann

Energy(الطاقة)	Microstates (الحالات المجهرية)					
	14		15		16	
2ε	b		a		ab	
ε	a		b		0	
0	0	0	0	0	0	0
$E_3 =$	3ε		3ε		$E_4 = 4\varepsilon$	

:

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$$\therefore g^N = (2+1+1)^2 = 4^2 = 16 \text{ microstates}$$

$$\begin{aligned} Z_{MB} &= \sum_{i=0} e^{-\beta E_i} \\ &= 4e^{-\beta E_0} + 4e^{-\beta E_1} + 5e^{-\beta E_2} + 2e^{-\beta E_3} + e^{-\beta E_4} \\ &= 4 + 4e^{-\beta\varepsilon} + 5e^{-2\beta\varepsilon} + 2e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon} \end{aligned}$$

:

$$\begin{aligned} \bar{E}_{MB} &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \\ &= \frac{4\varepsilon e^{-\beta\varepsilon} + 10\varepsilon e^{-2\beta\varepsilon} + 6\varepsilon e^{-3\beta\varepsilon} + 4\varepsilon e^{-4\beta\varepsilon}}{4 + 4e^{-\beta\varepsilon} + 5e^{-2\beta\varepsilon} + 2e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon}} \rightarrow \frac{3}{2} \varepsilon \quad (\text{as } T \rightarrow \infty) \end{aligned}$$

Classical Statistics of Maxwell-Boltzmann

$$Z_{\text{sp}} = \sum_i g_i e^{-\beta \varepsilon_i}$$

-1

Quantity	Symbol	Formula
	$U = N \bar{E} = N \left(\frac{\partial \ln Z_{\text{sp}}}{\partial \beta} \right)_{V,N}$	$Nk_B T^2 \left(\frac{\partial \ln Z_{\text{sp}}}{\partial T} \right)_{V,N}$
	$S = k_B \ln(\tilde{\omega})$	$Nk_B \ln Z_{\text{sp}} + \beta k_B U$
	$F = U - TS$	$-Nk_B T \ln Z_{\text{sp}}$
	$P = - \left(\frac{\partial F}{\partial V} \right)_{T,N}$	$Nk_B T \left(\frac{\partial \ln Z_{\text{sp}}}{\partial V} \right)_{T,N}$
	$\mu = - \left(\frac{\partial F}{\partial N} \right)_{T,V}$	$-Nk_B T \left(\frac{\partial \ln Z_{\text{sp}}}{\partial N} \right)_{V,T}$
	$G = F + PV$ $= F - V \left(\frac{\partial F}{\partial V} \right)_{T,N}$	$Nk_B T \left[\left(\frac{\partial \ln Z_{\text{sp}}}{\partial \ln U} \right)_{T,N} - \ln Z_{\text{sp}} \right]$
	$H = U + PV$	$Nk_B T \left[\left(\frac{\partial \ln Z_{\text{sp}}}{\partial \ln T} \right)_{V,N} + \left(\frac{\partial \ln Z_{\text{sp}}}{\partial \ln V} \right)_{T,N} \right]$
	$C_V = T \left(\frac{\partial S}{\partial T} \right)_{V,N}$ $= -T \left(\frac{\partial^2 F}{\partial T^2} \right)_{V,N}$	$Nk_B T \left[2 \left(\frac{\partial \ln Z_{\text{sp}}}{\partial T} \right)_V + T \left(\frac{\partial^2 \ln Z_{\text{sp}}}{\partial T^2} \right)_V \right]$

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$$\begin{aligned} \varepsilon_2 = 100 k_B \quad \varepsilon_1 = 0 & : & -2 \\ \cdot g_3 = 5 \quad g_2 = 3 \quad g_1 = 1 & & \varepsilon_3 = 200 k_B \\ .T = 100 \text{ K} & & \text{"Relative population"} \end{aligned}$$

$$: \quad (15) \quad :$$

$$\frac{n_j}{n_i} = \frac{g_j e^{-\beta \varepsilon_j}}{g_i e^{-\beta \varepsilon_i}} = \frac{g_j e^{-\beta \varepsilon_j}}{g_i e^{-\beta \varepsilon_i}}$$

$$\frac{n_2}{n_1} = \frac{3e^{-100k_B/100k_B}}{1e^{-0}} = 3e^{-1}$$

$$\frac{n_3}{n_1} = \frac{5e^{-200k_B/100k_B}}{1e^{-0}} = 5e^{-2}$$

$$\frac{n_3}{n_2} = \frac{5e^{-200k_B/100k_B}}{3e^{-100k_B/100k_B}} \approx 1.7e^{-1}$$

Classical Statistics of Maxwell-Boltzmann