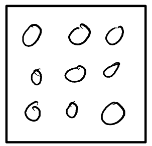
Sistema con 9 partículas:

T



Energía promedio total:

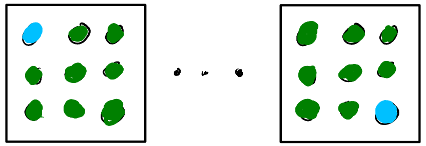
$U = \underbrace{n_1\varepsilon_1 + n_2\varepsilon_2}_{\text{energías}} = 20$

$\varepsilon_1 = 2$ $\quad\varepsilon_2 = 4$

Si: $n_1 = 8$, $n_2 = 1$:

$U = 8\cdot 2 + 1\cdot 4 = 9$ ✓

Posibles configuraciones:



$\Omega = 9$

*Principio de Boltzmann:

$$S = k_B \ln \Omega \quad (1.1)$$

Microestados: # configs. compatible con factores externos

$\Omega \geq 1 \rightarrow S \geq 0$ siempre

Si $n_1 = 9$ y $n_2 = 0$:

$\Omega = 1 \rightarrow S = k_B \ln(1)$

$S = 0$

*Postulado: El sistema debe

$$S_{max} \longleftrightarrow \Omega_{más} \quad (1.2)$$

Si el sistema puede estar en todos los estados posibles:

$$\Omega_1 < \Omega_2 < \Omega_3$$

$\downarrow$

Ω_{max}

es más probable que lo encontremos en Ω_{max}

partículas iguales

$\downarrow$

*Permutaciones con repetición:

Partículas con energ. $E_1 = n_1$

"

"

$E_M : n_M$

$+$

N

$$\Omega = \frac{N!}{n_1!\, n_2! \dots n_M!} \quad (1.3)$$

$$n_1 + \dots + n_M = N \quad (1.4)$$

$\rightarrow$ Macroestados

$$E_1 n_1 + \dots + E_M n_M = U \quad (1.5)$$

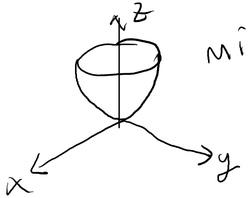
*Multiplicadores de Lagrange: para encontrar máximos o mínimos entre 3 superficies: $z(x,y)$, $g(x,y) = 0$, $h(x,y) = 0$

$$\mathcal{L} = z(x,y) - \alpha g(x,y) - \beta h(x,y) \quad (1.6)$$

$$\left.\begin{aligned} \frac{\partial \mathcal{L}}{\partial x} &= 0 \\ \frac{\partial \mathcal{L}}{\partial y} &= 0 \end{aligned}\right\} x_m, y_m \quad (1.7)$$

Ejm:

Paraboloide: $f = x^2 + y^2$



mínimo:

$x = 0$

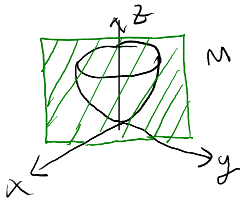
$y = 0$

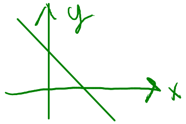
Si ahora agregamos el plano:

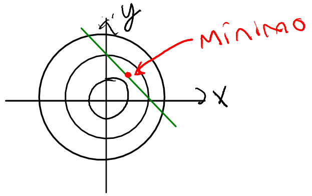
$x + 2y = 8 \rightarrow y = \frac{-x+8}{2}$

$\downarrow$

$g(x,y) = x + 2y - 8 = 0$







$$\mathcal{L} = (x^2+y^2) - \alpha(x+2y-8)$$

$\to \frac{\partial \mathcal{L}}{\partial x} = 2x_m - \alpha = 0 \qquad x_m = \alpha/2$

$\to \frac{\partial \mathcal{L}}{\partial y} = 2y_m - 2\alpha = 0 \qquad y_m = \alpha$

$\to x_m + 2y_m = 8$

$\alpha = 16/5$

Solución:

$x_m = \frac{\alpha}{2} = \frac{8}{5}$

$y_m = \alpha = 16/5$

* Formula de Stirling:

$$\ln n! \approx n\ln n - n \quad (1.8) \qquad n \to \infty$$

Para: $n_1 + n_2 = N$ cte

$n_1\varepsilon_1 + n_2\varepsilon_2 = U$ cte

$\left.\begin{matrix} n_1 = ? \\ n_2 = ? \end{matrix}\right\} S_{max}$

$$S = k\ln\Omega = k\ln\left(\frac{N!}{n_1!\,n_2!}\right)$$

$$S = k[\ln(N!) - \ln(n_1!) - \ln(n_2!)]$$

$$\frac{S}{k} = N\ln N - \cancel{N} - n_1\ln n_1 + \cancel{n_1} - n_2\ln n_2 + \cancel{n_2}$$

Intentando maximizar S:

$$\mathcal{L}(n_1,n_2) = k(N\ln N - n_1\ln n_1 - n_2\ln n_2) - \alpha(\underbrace{\text{Restricción 1}}_{n_1+n_2-N}) - \gamma(\underbrace{\text{Restricción 2}}_{n_1\varepsilon_1+n_2\varepsilon_2-U})$$

$\to \frac{\partial \mathcal{L}}{\partial n_1} = -k\ln n_1 - k - \alpha - \gamma\varepsilon_1 = 0$

$$n_1 = \underbrace{\exp\left(-1-\frac{\alpha}{k}\right)}_{A}\exp\left(-\underbrace{\frac{\gamma}{k}}_{\beta}\varepsilon_1\right)$$

$\to \frac{\partial \mathcal{L}}{\partial n_2} = 0$

$$n_2 = \underbrace{\exp\left(1-\frac{\alpha}{k}\right)}_{A}\exp(-\beta\varepsilon_2)$$

$\to n_1 + n_2 = N$

$$A(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}) = N$$

$\to n_1\varepsilon_1 + n_2\varepsilon_2 = U$

$$A(\varepsilon_1 e^{-\beta\varepsilon_1} + \varepsilon_2 e^{-\beta\varepsilon_2}) = U$$

$$\to \frac{U}{N} = \frac{\varepsilon_1 e^{-\beta\varepsilon_1} + \varepsilon_2 e^{-\beta\varepsilon_2}}{e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}}$$

$$U = \underbrace{\left(N\frac{e^{-\beta\varepsilon_1}}{e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}}\right)}_{n_1}\varepsilon_1 + \underbrace{\left(N\frac{e^{-\beta\varepsilon_2}}{e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}}\right)}_{n_2}\varepsilon_2$$

Probabilidad de que una partícula tenga la energía ε_1:

$$P_1 = \frac{n_1}{N} = \frac{e^{-\beta\varepsilon_1}}{e^{-\beta\varepsilon_1} + e^{-\varepsilon_2\beta}}$$

Probabilidad de que una partícula tenga la energía ε_2:

$$P_2 = \frac{n_2}{N} = \frac{e^{-\beta\varepsilon_2}}{e^{-\beta\varepsilon_1} + e^{-\varepsilon_2\beta}}$$

* Función de partición de una partícula (1.9)

$$Z_1 = e^{-\beta E_1} + \dots + e^{-\beta E_M} \qquad \beta = \frac{1}{k_B T}$$

* Probabilidad de tener n_i con energía E_i a S_{max}:

$$P_i = \frac{n_i}{N} = \frac{e^{-\beta E_i}}{Z_1} \quad (1.10)$$

$$\to -\frac{1}{Z_1}\frac{\partial Z_1}{\partial\beta} = -\frac{1}{Z_1}\frac{\partial}{\partial\beta}(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2})$$

$$= \frac{\varepsilon_1 e^{-\beta\varepsilon_1} + \varepsilon_2 e^{-\beta\varepsilon_2}}{e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}}$$

$$-\left(\frac{\partial \ln Z_1}{\partial\beta}\right) = \left(\frac{U}{N}\right)$$

$$U = -\frac{\partial N\ln Z_1}{\partial\beta} = -\frac{\partial \ln Z_1^N}{\partial\beta}$$

* Función de partición para N partículas:

$$Z = Z_1^N \qquad (1.11)$$

* Energía interna total:

$$U = -\frac{\partial}{\partial \beta}\ln Z \qquad (1.12)$$

$$\to \frac{S}{K} = N\ln N - \underbrace{n_1 \ln n_1}_{Np_1} - \underbrace{n_2 \ln n_2}_{Np_2}$$

$$\frac{S}{KN} = \cancel{\ln N} - p_1 \cancel{\ln N} - p_1 \ln p_1 - p_2 \cancel{\ln N} - p_2 \ln p_2$$

$$(\ln N)(\cancel{1 - p_1 - p_2}) \to 0$$

$$S = N k_B(-p_1 \ln p_1 - p_2 \ln p_2)$$

$$\boxed{(1.10) \to p_i = \frac{e^{-\beta\varepsilon_i}}{Z_1}}$$

$$S = \frac{N k_B}{Z_1}\left(\beta\varepsilon_1 e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_1}\ln Z_1 + \beta\varepsilon_2 e^{-\beta\varepsilon_2} + e^{-\beta\varepsilon_2}\ln Z_1\right)$$

$$\to Z_1 \ln Z_1$$

$$S = N k_B\left(\beta\underbrace{\frac{\varepsilon_1 e^{-\beta\varepsilon_1} + \varepsilon_2 e^{-\beta\varepsilon_2}}{Z_1}}_{U/N} + \ln Z_1\right)$$

$$S = k_B \beta U + k_B \ln Z_1^N \to Z$$

* Entropía: (1.13) ← (1.12)

$$S = -k_B\beta\frac{\partial \ln Z}{\partial \beta} + k_B \ln Z$$

* Primer principio de la termo. con N cte:

$$dU = TdS - Pd\forall \qquad (1.14)$$

$$\to T = \left(\frac{\partial U}{\partial S}\right)_{\forall} \qquad \to P = -\left(\frac{\partial U}{\partial \forall}\right)_{S} \qquad (1.15)$$

cte   cte

Usando (1.13):

$$S = k_B\beta U + k_B \ln Z$$

$$U = \frac{S - k_B \ln Z}{k_B \beta}$$

Si $\forall$ es cte:

$$\to \left(\frac{\partial U}{\partial S}\right)_{\forall} = \frac{1}{k_B\beta} = T \leftarrow (1.15)$$

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

* Energía libre de Helmholtz:

$$A = U - TS \qquad (1.16)$$

$$U \to -\frac{\partial \ln Z}{\partial \beta} \qquad TS \to -k_B\beta\frac{\partial \ln Z}{\partial \beta} + k_B \ln Z, \quad \beta \to 1/k_B T$$

$$A = -\frac{\ln Z}{\beta} \qquad (1.17)$$

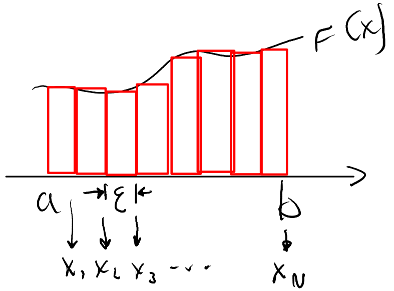
* Cambio de la energía libre de Helmholtz:

$$dA = -SdT - Pd\forall \qquad (1.18)$$

Si T es cte:

$$P = -\left(\frac{\partial A}{\partial \forall}\right)_T \qquad (1.19)$$

$$P = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial \forall}\right)_T \qquad (1.20)$$



$$\to \varepsilon = \frac{b-a}{N} \qquad \to x_n = a + n\varepsilon \qquad \to x_N = a + N\varepsilon$$

$$x_N = a + (b-a) = b \checkmark$$

$$\to A \simeq \sum_{n=0}^{N} \varepsilon F(x_n) = \varepsilon\sum_{n=0}^{N} F(a+n\varepsilon)$$

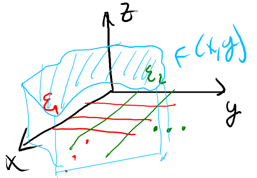
Cuando $\varepsilon \to 0$

$$\int_a^b F(x)dx \simeq \varepsilon \sum_{n=0}^{N} F(a+n\varepsilon)$$

$$\sum_{n=0}^{N} F(a+n\varepsilon) \simeq \frac{1}{\varepsilon}\int_a^b F(x)dx \qquad (2.1)$$

Para el V bajo la superficie:

$F(x,y)$:



→ $\varepsilon_1 \varepsilon_2 \sum_{n=0}^{N} \sum_{m=0}^{M} F(x_n, y_m)$

$$\simeq \int_{a_x}^{b_x} \int_{a_y}^{b_y} F(x,y)\,dx\,dy$$

$$\sum_{n=0}^{N} \sum_{m=0}^{M} F(x_n, y_m) \simeq \frac{1}{\varepsilon_1 \varepsilon_2} \int_{a_x}^{b_x} \int_{a_y}^{b_y} F(x,y)\,dx\,dy \qquad (2.2)$$

Approx. de series con integrales; n, M y $p = 0, 1, 2, \dots, N$

$N \to \infty$

$\varepsilon_1 = x_1 - x_0 = x_2 - x_1 = \dots$

$\varepsilon_2 = y_1 - y_0 = y_2 - y_1 = \dots$

$\varepsilon_3 = z_1 - z_0 = z_2 - z_1 = \dots$

$$\sum_{n}^{N} \sum_{m}^{N} \sum_{p}^{N} F(x_n, y_m, z_p) \qquad (2.3)$$

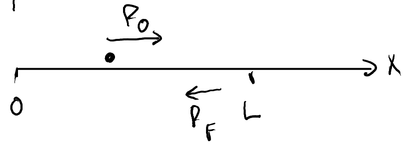
$$\approx \frac{1}{\varepsilon_1 \varepsilon_2 \varepsilon_3} \int_{x_0}^{x_N} \int_{y_0}^{y_N} \int_{z_0}^{z_N} F(x,y,z)\,dx\,dy\,dz$$

→ Energía de una partícula en un campo conservativo:

$$E = \frac{p^2}{2m} + E_p(x) \qquad (3.1)$$

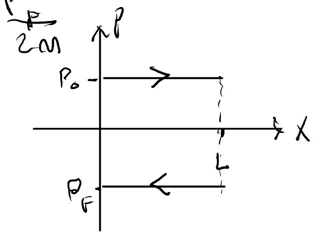
→ Espacio de fases: cant. de mov (posición) = $p(x)$

Ex: partícula q' se mueve a p cte y rebota en L elásticamente:



→ $E_0 = \frac{P_0^2}{2m} = E_F = \frac{P_F^2}{2m}$

→ $P_F = -P_0$



No interactúa con las fronteras

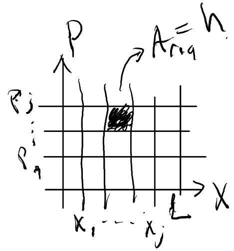
→ Partícula libre en una caja de tamaño L en 1D:

→ $\varepsilon = \sqrt{h}$

$\varepsilon^2 = h$

→ $x_i = i\varepsilon = i\sqrt{h}$

→ $p_j = j\varepsilon = j\sqrt{h}$



→ $E_{ij}^{1D} = \frac{p_j^2}{2m}$ (3.2)

→ $Z_1 = \sum_i \sum_j e^{-\beta E_{ij}} = \sum_i \sum_j e^{-\beta \frac{p_j^2}{2m}}$

De discreto a continuo: ← (2.3)

$$Z_1 \approx \underbrace{\frac{1}{\varepsilon^2} \int_0^L dx}_{L/h} \int_{-\infty}^{\infty} dp\, e^{-\beta p^2/2m}$$

$L >> h$

Si: $t = \sqrt{\frac{\beta}{2m}}\, p$

$dp = \sqrt{\frac{2m}{\beta}}\, dt$

→ Integral de Gauss:

$$\int_{-\infty}^{\infty} dt\, e^{-t^2} = \sqrt{\pi} \qquad (3.3)$$

→ $Z_1^{1D} = \frac{L}{h} \sqrt{\frac{2m\pi}{\beta}}$ (3.4)

→ $U = -\frac{\partial}{\partial \beta} \ln Z$ ← (1.12)

Una partícula:

$U_1 = -\frac{\partial}{\partial \beta} \ln Z_1$

$\ln\left(\frac{L}{h}\right) + \frac{1}{2}\ln(2m\pi) - \frac{1}{2}\ln\beta$

$U_1^{1D} = \frac{1}{2\beta} = \frac{1}{2} K_B T$

$L >> \sqrt{h}$

$-\infty < p < \infty$

↳ Energía promedio (3.5)

→ Partícula libre en una caja de tamaño V en 3D:

$$E_i = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \quad (4.1)$$

$$h^3 = \underbrace{(\Delta p_x \Delta x)(\Delta p_y \Delta y)(\Delta p_z \Delta z)}_{\text{espacio de fases}} \quad (4.2)$$

$$Z_1^{3D} = Z_1 = \frac{V}{h^3}\left(\sqrt{\frac{2m\pi}{\beta}}\right)^3 \quad (4.3)$$

$$U_1 = \frac{3}{2\beta} = \frac{3}{2}k_B T \quad (4.4)$$

Energía promedio

→ N partículas libres e idénticas no interactuantes

$$Z_N^{3D} = \frac{(Z_1^{3D})^N}{N!} \quad (4.5)$$

Gases ideales

$$Z_N^{3D} = Z_N = \frac{(Z_1^{3D})^N}{N!} \quad (4.6)$$

$$P = \frac{k_B T N}{V} \quad (5.1)$$

Usando $PV = nRT$:

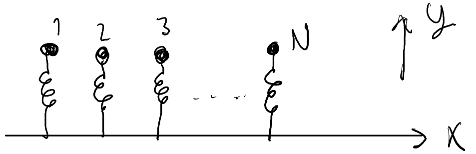
$$nR = k_B N \quad (5.2)$$

$$U = \frac{3N}{2}k_B T = \frac{3}{2}nRT \quad (5.3)$$

$$S = nR\ln V + \frac{3}{2}nR\ln k_B T - k_B \ln N! + \frac{3nR}{2}\ln\frac{2m\pi}{h^2} + \frac{3nR}{2} \quad (5.4)$$

$$dS = nR\frac{dV}{V} + \frac{3}{2}nR\frac{dT}{T} \quad (5.5)$$

Función de partición para N osciladores en equilibrio térmico T:



$\to Z = Z_1^N$ (6.1)

→ Son distinguibles

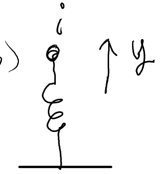
↑

posiciones x determinadas

$\to U = N k_B T$ (6.2)

Para un oscilador:

$$\to E_i = \frac{p_i^2}{2m} + \frac{m\omega^2}{2} y_i^2 \quad (6.3)$$



$$\to Z_1 = \frac{1}{h}\frac{2\pi}{\beta\omega} \quad (6.4)$$

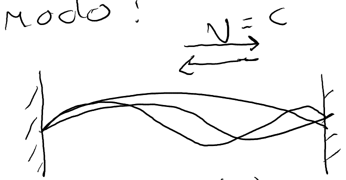
↗

$\Delta p \Delta x$

↑ space de fases

$\to U_1 = k_B T$ (6.5)

Onda estacionaria en n modo:



$\to y = y_0(t) \sin k_n x$ (6.6)

$\to k_n = \frac{n\pi}{L}$ (6.7) $\to \omega_n = k_n c$ (6.8)

Para N osciladores vibrando a n modo normal:

$$\to y = \left(A \sin \frac{n\pi}{L} x\right) \cos \omega t \quad (6.9)$$

Catastrofe ultravioleta:

$$\to U_{total} = N k_B T \sum_{n=1}^{\infty} 1 \quad (6.10)$$

↑

infinitos modos normales

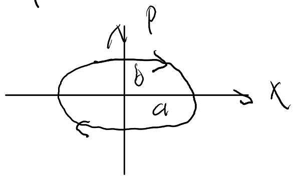
Para un oscilador clásico a energía cte E: (7.1)

$$1 = \left(\frac{x}{\frac{1}{\omega}\sqrt{\frac{E}{m}}}\right)^2 + \left(\frac{p}{\sqrt{2mE}}\right)^2$$

Ec. elipse:

$$1 = \left(\frac{x}{a}\right)^2 + \left(\frac{p}{b}\right)^2 \quad (7.2)$$

En el espacio de fases:



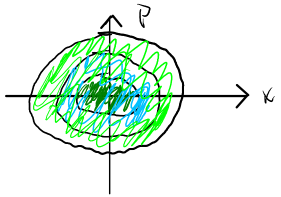
$$A = \frac{2\pi E}{\omega} \quad (7.3)$$

Hipotesis de Planck (a nivel quant.):

$A_{min} = h$

$A_2 = 2h$

$A_3 = 3h$



$$E_n = n\frac{h}{2\pi}\omega = n\hbar\omega \quad n = 1, 2, 3, \ldots \quad (7.4)$$

Realmente es un oscilador armónico cuántico: (7.5)

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \quad n = 0, 1, 2, \ldots$$

$\uparrow$ modos de vibrac.

Para el osc. armónico cuántico a T:

$$Z = \sum_{m} e^{-\beta\hbar\omega m} = \frac{1}{1 - e^{-\beta\hbar\omega}} \quad (8.1)$$

m $\rightarrow$ modos de vibración

$$U = -\frac{\partial \ln Z}{\partial \beta} = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \quad (8.2)$$

Oscilador clásico: (8.4) Taylor

$\rightarrow T \rightarrow \infty \Rightarrow \beta \simeq 0 \rightarrow e^{\beta\hbar\omega} \approx 1 + \beta\hbar\omega$

$\rightarrow U = k_B T$ (8.3)

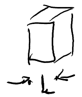
Oscilador quantum a $T \simeq 0$:

$\rightarrow \beta \rightarrow \infty \rightarrow U = 0$ (8.5)

mínima U realmente es

$$U = \frac{1}{2}\hbar\omega \quad (8.6)$$

Cavidad electromagnética:



En las paredes:

$$\underbrace{\underset{\text{Transversal}}{E_T = 0} \quad \underset{\text{normal}}{B_n = 0}}_{\vec{E},\ \vec{B} \leftarrow \text{Maxwell}} \quad (8.7)$$

$$\vec{E} = \vec{E}(\vec{r}, t, \omega, \underbrace{m_x, m_y, m_z}_{\text{modos de vibra.} \rightarrow \vec{m}}) \quad (8.8)$$

Para el modo de vibración m:

$$\omega_m = \underbrace{\frac{\pi}{L}\sqrt{m_x^2 + m_y^2 + m_z^2}}_{|\vec{k}_m|} \cdot c \quad (8.9)$$

$$U_m = \frac{\hbar\omega_m}{e^{\beta\hbar\omega_m} - 1} \quad (8.10)$$

Energía promedio total: (8.11)

$$U = \sum_{m_x}\sum_{m_y}\sum_{m_z} U_m = \frac{L^3\pi^2}{15(\hbar c)^3\beta^4}$$

Ley de Stefan-Boltzman:

Densidad de energía:

$$u = \frac{U}{L^3} = \frac{\pi^2 k_B^4}{15(\hbar c)^3} T^4 \quad (8.12)$$

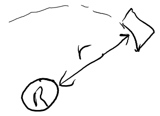
Potencia emisiva hemisférica total:

$$W = \frac{c}{4}u = \frac{2\pi^5 k_B^4}{15 c^2 h^3} T^4$$

$$W = \sigma T^4 \quad (9.5)$$

$$[W] = \frac{\text{watt}}{m^2}$$

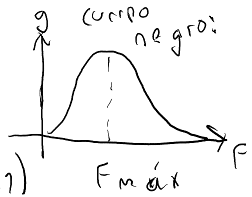
Intensidad a una distancia r de un cuerpo negro con radio R: (9.6)



$$I = \frac{\sigma T^4 R^2}{r^2} < \sigma T^4$$

Ley de Planck:

$$g = \frac{2\pi h}{c^2}\,\frac{F^3}{e^{\beta h F}-1} \qquad (9.1)$$



$$\left.\frac{dg}{dF}\right|_{F_{max}} = 0 \qquad (9.2) \quad \rightarrow [g] = \frac{J}{m^2}$$

$$\rightarrow F_{max} = \frac{2.822}{h}\,k_B T \qquad (9.3)$$

$$\rightarrow \lambda_{max} = \frac{c}{F_{max}} = \frac{0.0028976\,mK}{T} \qquad (9.4)$$