Mecânica Estatística
Lista-3

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1 Reif – Fundamentals of Statistical and Thermal Physics

7.2) An ideal monatomic gas of N. particles, each of mass m, is in thermal equilibrium at absolute temperature T. The gas is contained in a cubical box of side L, whose top and bottom sides are parallel to the earth's surface. The effect of the earth's uniform gravitational field on the particles should be considered the acceleration due to gravity being g.

(a) what is the average kinetic energy of a particle?

(b) what is the average potential energy of a particle?

....:: solução ::...

Item (a) what is the average kinetic energy of a particle?

Do teorema da equipartição da energia, obtemos diretamente a energia cinética média $\bar{\mathcal{T}}$

$$\bar{\mathcal{T}} = \frac{1}{2}kT, \quad \text{para um grau de liberdade}$$
$$\bar{\mathcal{T}} = \frac{3}{2}kT, \quad \text{para três grau de liberdade} \tag{1.1}$$

Item (b) what is the average potential energy of a particle?

Usando a função de partição,

$$Z = \sum_r e - \beta E_r \tag{1.2}$$

7.2

(a) Do teorema da equipartição da energia, obtemos

$\overline{T} = \frac{1}{2} kT$, um grau de liberdade

$\overline{T} = \frac{3}{2} kT$, três graus de liberdade

(b) Usando a função de Partição

$$Z = \sum_r e^{-\beta E_r} \longrightarrow Z = \int dp\,dq\, e^{-\beta E_r}$$

$$E = \sum_{k=1}^{N} \left(\frac{\vec{p}_k^{\,2}}{2m} + mgz_k \right)$$; uma partícula temos,

$$Z = \frac{1}{2\pi h_0} \frac{1}{N!} \int dp\,dq\, e^{-\left(\frac{\vec{p}^{\,2}}{2m} + mgz\right)}$$

$$= \frac{1}{2\pi h_0} \frac{1}{N!} \int dp_x dp_y dp_z dq_x dq_y dq_z\, e^{-\left(\frac{\vec{p}^{\,2}}{2m} + mgz\right)}$$

$$= \frac{1}{2\pi h_0} \frac{1}{N!} \int_0^L\!\!\int_0^L\!\!\int_0^L dp_x dp_y dp_z\, e^{-\left(\beta\frac{\vec{p}^{\,2}}{2m}\right)} \underbrace{\int_0^L\!\!\int_0^L\!\!\int_0^L dq_x dq_y dq_z\, e^{-\beta(mgz)}}_{(\dots)}$$

$$= \frac{1}{2\pi h_0} \frac{1}{N!} \left(2\pi m \frac{1}{\beta}\right)^{3/2} \int\!\!\int\!\!\int_0^L (\dots)$$

$$Z = \frac{1}{2\pi\hbar_0}\frac{1}{N!}\left(\frac{2\pi m}{\beta}\right)^{3/2}\int_0^L dx\int_0^L dy\int_0^L dz\, e^{-\beta(mgz)}$$

$$= \frac{1}{2\pi\hbar_0}\frac{1}{N!}\left(\frac{2\pi m}{\beta}\right)^{3/2}L^2\int_0^L dz\, e^{-\beta mgz}$$

$$= \frac{1}{2\pi\hbar_0}\frac{1}{N!}\left(\frac{2\pi m}{\beta}\right)^{3/2}L^2\left[\frac{e^{-\beta mgz}}{-\beta mg}\right]\Bigg|_{z=0}^{L}$$

$$= \frac{1}{2\pi\hbar_0}\frac{1}{N!}\left(\frac{2\pi m}{\beta}\right)^{3/2}L^2\left[\frac{e^{-\beta mgL}}{-\beta mg}+\frac{e^{-\beta mg(0)}}{\beta mg}\right]$$

$$= \frac{1}{2\pi\hbar_0}\frac{1}{N!}\left(\frac{2\pi m}{\beta}\right)^{3/2}L^2\left[\frac{1}{\beta mg}-\frac{e^{-\beta mgL}}{\beta mg}\right]$$

$$= \frac{1}{2\pi\hbar_0}\frac{1}{N!}\left(\frac{2\pi m}{\beta}\right)^{3}\frac{L^2}{\beta mg}\left(1-e^{-\beta mgL}\right)$$

$$\boxed{Z = \frac{(2\pi m/\beta)^{3/2}}{2\pi\hbar_0 N!}\cdot\frac{L^2}{mg\beta}\left(1-e^{-\beta mgL}\right)}$$

$$\bar{V} = \frac{\int dp\,dq\, e^{-\beta\left(\vec{p}^{\,2}/2m + mgz\right)}(mgz)}{Z}$$

$$= \frac{1}{Z}\int_0^L\!\!\int_0^L\!\!\int_0^L dp_x\,dp_x\,dp_z\, e^{-\beta\frac{\vec{p}^{\,2}}{2m}}\int_0^L\!\!\int_0^L\!\!\int_0^L mgz\, e^{-\beta mgz}\,dx\,dy\,dz$$

$$\overline{V} = \left(\frac{2\pi m}{\beta}\right)^{3/2} \frac{L^2}{Z} \int_0^L mgz\, e^{-\beta mgz} dz$$

Partes $\int w\,dv = wv - \int v\,dw$

$w = z \rightarrow dw = dz$

$dv = e^{-\beta mgz} \rightarrow v = \frac{e^{-\beta mgz}}{-\beta mg}$

$$= \left(\frac{2\pi m}{\beta}\right)^{3/2} \frac{L^2}{Z} mg \left[-\frac{z}{\beta mg} e^{-\beta mgz} \Big|_{z=0}^{L} + \frac{1}{\beta mg} \int_0^L e^{-\beta mgz} dz \right]$$

$$= (2\pi m/\beta)^{3/2} \frac{L^2}{Z} mg \left[-\frac{L}{\beta mg} e^{-\beta mgL} - \frac{1}{(\beta mg)^2} e^{-\beta mgz} \Big|_{z=0}^{L} \right]$$

$$= (2\pi m/\beta)^{3/2} \frac{L^2}{Z} mg \left[-\frac{L}{\beta mg} e^{-\beta mgL} - \frac{1}{(\beta mg)^2} \left(e^{-\beta mgL} - 1 \right) \right]$$

$$= (2\pi m/\beta)^{3/2} \frac{L^2}{Z} mg \left[-\frac{\beta mgL}{(\beta mg)^2} e^{-\beta mgL} + \frac{1}{(\beta mg)^2} \left(1 - e^{-\beta mgL} \right) \right]$$

$$= (2\pi m/\beta)^{3/2} \frac{L^2}{Z} mg \, \frac{-\beta mgL\, e^{-\beta mgL} + 1 - e^{-\beta mgL}}{\beta^2 (mg)^2}$$

$$= (2\pi m/\beta)^{3/2} \frac{L^2}{Z \beta^2 mg} \left[-e^{-\beta mgL} \left(\beta mgL + e^{\beta mgL} + 1 \right) \right]$$

$$= (2\pi m/\beta)^{3/2} \frac{L^2}{Z \beta^2 mg} \left[e^{-\beta mgL} \left(e^{+\beta mgL} - \beta mgL - 1 \right) \right]$$

$$\bar{V} = \frac{1}{Z} \left(2\pi m/\beta\right)^{3/2} \frac{L^2}{mg\beta^2} \left[e^{-\beta mgh}\left(e^{\beta mgh} - \beta mgh - 1\right)\right]$$

$$= \text{[crossed out]}$$

$$= \underbrace{\left[\frac{(2\pi h_0 N!)}{(2\pi m/\beta)^{3/2}} \frac{\beta mg}{L^2} \frac{1}{(1-e^{-\beta mgh})}\right]}_{= \frac{1}{Z}} \left(2\pi m/\beta\right)^{3/2} \frac{L^2}{mg\beta^2} \left[e^{-\beta mgh}\left(e^{+\beta mgh} - mgh\beta - 1\right)\right]$$

$$= \underbrace{(2\pi h_0 N!)}_{= \Omega} \frac{1}{\beta} \left[e^{-\beta mgh}\left(e^{\beta mgh} - \beta mgh - 1\right)\right]$$

$$\boxed{\bar{V} = \frac{\Omega}{\beta} - \frac{\Omega mgh}{e^{-\beta mgh} - 1}}$$

onde $\Omega = 2\pi h_0 N!$

7.3) A thermally insulated container is divided by a partition into two compartments, the right compartment having a volume b times as large as the left one. The left compartment contains ν moles of an ideal gas at temperature T and pressure $\bar{p}$. The right compartment also contains ν moles of an ideal gas at the teperature T. The partition is now removed. Calculate

(a) the final pressure of the gas mixture in terms of $\bar{p}$;

(b) the total change of entropy if the gases are different;

(c) the total change of entropy if the gases are identical;

....:: Solução ::..

Item (a) the final pressure of the gas mixture in terms of $\bar{p}$

Os dois compartimentos estão a mesma temperatura T, portanto

$$\frac{\bar{p}V}{\nu R} = \frac{pV(1+b)}{2\nu R} \quad \longrightarrow \quad p = 2\bar{p}\,(1+b)^{-1} \tag{1.3}$$

Item (b) the total change of entropy if the gases are different

Temos dois gases A e B. Vamos supor que o compartimento da esquerda contém o gás A e o da direita o gás B. Como o gás A é diferente do gás $B \longrightarrow m_A \neq m_B$.

Entropia

$$S = Nk\left[ln\frac{V}{N} + \frac{3}{2}lnT + \frac{3}{2}ln\left(\frac{2\pi mk}{h_0^2}\right) + \frac{5}{2}\right] \tag{1.4}$$

Inicialmente o container está dividido em dois compartimentos, então a entropia inicial S_i é a soma das entropias dos gases dos compartimentos da esquerda $S_{i\text{A}}$ e da direita $S_{i\text{B}}$.

$$\begin{aligned}
S_{i\text{A}} &= Nk\left[ln\frac{V}{N} + \frac{3}{2}lnT + \frac{3}{2}ln\left(\frac{2\pi m_{\text{A}}k}{h_0^2}\right) + \frac{5}{2}\right] && (1.5)\\
S_{i\text{B}} &= Nk\left[ln\frac{Vb}{N} + \frac{3}{2}lnT + \frac{3}{2}ln\left(\frac{2\pi m_{\text{B}}k}{h_0^2}\right) + \frac{5}{2}\right] && (1.6)\\
S_{i\text{A}} + S_{i\text{B}} &= Nk\left[ln\frac{V}{N} + \frac{3}{2}lnT + \frac{3}{2}ln\left(\frac{2\pi m_{\text{A}}k}{h_0^2}\right) + \frac{5}{2} + ln\frac{Vb}{N} + \frac{3}{2}lnT + \frac{3}{2}ln\left(\frac{2\pi m_{\text{B}}k}{h_0^2}\right) + \frac{5}{2}\right]\\
&= Nk\left[ln\frac{V^2b}{N^2} + 3\,lnT + 3\,ln\left(\frac{2\pi\sqrt{m_{\text{A}}m_{\text{B}}}k}{h_0^2}\right) + 5\right] && (1.7)\\
&= S_i && (1.8)
\end{aligned}$$

Quando o a divisão é removida os dois gases ocupam todo o volume do container e a entropia final S_f é a soma das entropias dos dois gases $S_{f\text{A}}$ e $S_{f\text{B}}$, considerando o volume total.

$$\begin{aligned}
S_{f\text{A}} &= kN\left[ln\frac{V(1+b)}{N} + \frac{3}{2}lnT + \frac{3}{2}ln\left(\frac{2\pi m_{\text{A}}k}{h_0^2}\right) + \frac{5}{2}\right] && (1.9)\\
S_{f\text{B}} &= kN\left[ln\frac{V(1+b)}{N} + \frac{3}{2}lnT + \frac{3}{2}ln\left(\frac{2\pi m_{\text{B}}k}{h_0^2}\right) + \frac{5}{2}\right] && (1.10)\\
S_{f\text{A}} + S_{f\text{B}} &= kN\left[ln\frac{V^2(1+b)^2}{N^2} + 3\,lnT + 3\,ln\left(\frac{2\pi\sqrt{m_{\text{A}}m_{\text{B}}}k}{h_0^2}\right) + 5\right] && (1.11)\\
&= S_f && (1.12)
\end{aligned}$$

Por fim, temos

$$
\begin{aligned}
\Delta S &= S_f - S_i \\
&= kN\left\{ln\frac{V^2(1+b)^2}{N^2} + 3\,lnT + 3\,ln\left(\frac{2\pi\sqrt{m_A m_B}k}{h_0^2}\right) + 5 - ln\frac{V^2b}{N^2} - 3\,lnT - 3\,ln\left(\frac{2\pi\sqrt{m_A m_B}k}{h_0^2}\right) - 5\right\} \\
&= kN\left\{ln\frac{V^2(1+b)^2}{N^2} - ln\frac{V^2b}{N^2}\right\} \\
&= kN\left\{ln\left[\frac{N^2V^2(1+b)^2}{N^2V^2b}\right]\right\} \\
&= kNln\left[\frac{(1+b)^2}{b}\right], \quad \text{como} \quad k = \frac{R}{N_A} \quad \text{e} \quad N = \nu N_A \\
&= \nu R\, ln\left[\frac{(1+b)^2}{b}\right] \qquad (1.13)
\end{aligned}
$$

Item (c) the total change of entropy if the gases are identical

Temos dois gases A e B. Novamente vamos supor que o compartimento da esquerda contém o gás A e o da direita o gás B. Como o gás A é igual ao gás $B \longrightarrow m_A = m_B = m$.

<u>**Entropia**</u>

$$
S = Nk\left[ln\frac{V}{N} + \frac{3}{2}lnT + \frac{3}{2}ln\left(\frac{2\pi mk}{h_0^2}\right) + \frac{5}{2}\right] \qquad (1.14)
$$

Inicialmente o container está dividido em dois compartimentos, então a entropia inicial S_i é a soma das entropias dos gases dos compartimentos da esquerda S_{iA} e da direita S_{iB}.

$$
\begin{aligned}
S_{iA} &= Nk\left[ln\frac{V}{N} + \frac{3}{2}lnT + \frac{3}{2}ln\left(\frac{2\pi mk}{h_0^2}\right) + \frac{5}{2}\right] \qquad (1.15) \\
S_{iB} &= Nk\left[ln\frac{Vb}{N} + \frac{3}{2}lnT + \frac{3}{2}ln\left(\frac{2\pi mk}{h_0^2}\right) + \frac{5}{2}\right] \qquad (1.16) \\
S_{iA} + S_{iB} &= Nk\left[ln\frac{V}{N} + \frac{3}{2}lnT + \frac{3}{2}ln\left(\frac{2\pi mk}{h_0^2}\right) + \frac{5}{2} + ln\frac{Vb}{N} + \frac{3}{2}lnT + \frac{3}{2}ln\left(\frac{2\pi mk}{h_0^2}\right) + \frac{5}{2}\right] \\
&= Nk\left[ln\frac{V^2b}{N^2} + 3\,lnT + 3\,ln\left(\frac{2\pi mk}{h_0^2}\right) + 5\right] \qquad (1.17) \\
&= S_i \qquad (1.18)
\end{aligned}
$$

Quando o a divisão é removida os dois gases ocupam todo o volume do container, porém agora estamos falando do mesmo gás (não há distinção) então $N \longrightarrow 2N$ e a entropia final é simplesmente S_f.

$$
\begin{aligned}
S_f &= 2Nk\left[ln\frac{V(1+b)}{2N} + \frac{3}{2}lnT + \frac{3}{2}ln\left(\frac{2\pi mk}{h_0^2}\right) + \frac{5}{2}\right] \qquad (1.19) \\
&= Nk\left[ln\frac{V^2(1+b)^2}{4N^2} + 3\,lnT + 3\,ln\left(\frac{2\pi mk}{h_0^2}\right) + 5\right] \qquad (1.20)
\end{aligned}
$$

(1.20)

Por fim, temos

$$
\begin{aligned}
\Delta S &= S_f - S_i \\
&= Nk\left\{ ln\frac{V^2(1+b)^2}{4N^2} + 3\,lnT + 3\,ln\left(\frac{2\pi mk}{h_0^2}\right) + 5 - ln\frac{V^2b}{N^2} - 3\,lnT - 3\,ln\left(\frac{2\pi mk}{h_0^2}\right) - 5 \right\} \\
&= kN\left\{ ln\frac{V^2(1+b)^2}{N^2} - ln\frac{V^2b}{N^2} \right\} \\
&= kN\left\{ ln\left[\frac{N^2V^2(1+b)^2}{4N^2V^2b}\right] \right\} \\
&= kN ln\left[\frac{(1+b)^2}{4b}\right], \quad \text{como} \quad k = \frac{R}{N_A} \quad \text{e} \quad N = \nu N_A \\
&= \nu\, R\, ln\left[\frac{(1+b)^2}{4b}\right] \qquad (1.21)
\end{aligned}
$$

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7.10) A system consists of N very weakly interacting particles at a temperature T sufficiently high so that classical statistical mechanics is applicable. Each particle has mass m and is free to perform one-dimensional oscillations about its equilibrium position. Calculate the heat capacity of this system of particles at this temperature in each of the following cases:

(a) the force effective in restoring each particle to its equilibrium position is proportional to its displacement x from this position.

(b) the restoring force is proportional x^3.

....:: solução ::..

Do teorema do Virial, se a energia potencial de cada partícula é $\mathcal{V} \propto x^n$, então energia Cinética $\bar{\mathcal{T}}$ e a energia potencial $\bar{\mathcal{V}}$ satisfaz a relação

$$n\bar{\mathcal{V}} = 2\bar{\mathcal{T}} \tag{1.22}$$

Do teorema da equipartição da energia temos

$$\bar{\mathcal{T}} = \frac{1}{2}kT \tag{1.23}$$

Item (a)

força $\propto x$ e $\mathcal{V} \propto x^2$, podemos obter a energia $\bar{E}$ usando (1.22) e (1.23), lembrando que $n = 2$

$$\bar{\mathcal{V}} = \bar{\mathcal{T}} = \frac{1}{2}kT \quad \longrightarrow \quad \bar{E} = \bar{\mathcal{V}} + \bar{\mathcal{T}} = kT \tag{1.24}$$

$$C_v = (\frac{\partial \bar{E}}{\partial T})_v = k, \quad \text{para uma partícula} \tag{1.25}$$

$$C_v = Nk, \quad \text{para o sistema} \tag{1.26}$$

Item (b)

força $\propto x^3$ e $\mathcal{V} \propto x^4$, procedendo de modo análogo ao feito no item (a), mas agora com $n = 4$

$$\bar{\mathcal{V}} = \frac{1}{2}\bar{\mathcal{T}} = \frac{1}{4}kT \quad \longrightarrow \quad \bar{E} = \bar{\mathcal{V}} + \bar{\mathcal{T}} = \frac{1}{4}kT + \frac{1}{2}kT = \frac{3}{4}kT \tag{1.27}$$

$$C_v = (\frac{\partial \bar{E}}{\partial T})_v = \frac{3}{4}k, \quad \text{para uma partícula} \tag{1.28}$$

$$C_v = \frac{3}{4}Nk, \quad \text{para o sistema} \tag{1.29}$$

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7.14) Consider an assembly of N_0 weakly interacting magnetic atoms per unit volume at temperature T and describe the situation *classically*. Then each magnetic moment $\mathbf{u}$ can make any arbitrary angle θ with respect to a given direction (call it the z direction). In the absence of a magnetic field, the probability that this angle lies between θ and $\theta+d\theta$ is simply proportional to the solid angle $2\pi\sin\theta\, d\theta$ enclosed in this range. In the presence of a magnetic field H in the z direction, this probability must further be proportional to the Boltzmann factor $e^{-\beta E}$, where E is the magnetic energy of the moment $\mathbf{u}$ making this angle θ with the z axis. Use this result to calculate the classical expression for the mean magnetic moment $\bar{M}_z$ of these N_0 atoms.

....:: solução ::...

A probabilidade $P(\theta)$ para momento atômico com um ângulo $\theta \in [\theta, \theta + d\theta]$,

$$P(\theta) \propto 2\pi \sin\theta d\theta\, e^{-\beta E} \tag{1.30}$$

A energia magnética é dada por

$$E = \mathbf{u}\cdot\mathbf{H} = uH\cos\theta \tag{1.31}$$

O momento magnético médio $\bar{M}_z$ do sistema na direção z

$$\bar{M}_z = \frac{\int_0^\pi N_0 u\cos\theta\, e^{\beta uH\cos\theta}\sin\theta d\theta}{\int_0^\pi e^{\beta uH\cos\theta}\sin\theta d\theta} \tag{1.32}$$

$$= N_0 u\frac{\int\cos\theta\, e^{\beta uH(\cos\theta)}d(\cos\theta)}{\int e^{\beta uH(\cos\theta)}d(\cos\theta)} \quad \text{limites de integração} \quad \cos\pi = -1 \quad \text{e} \quad \cos 0 = 1$$

$$= N_0 u\frac{\frac{1}{uH}\int\frac{\partial}{\partial\beta}e^{\beta uH(\cos\theta)}d(\cos\theta)}{\int e^{\beta uH(\cos\theta)}d(\cos\theta)} \tag{1.33}$$

$$= N_0 u\frac{\frac{1}{uH}\frac{\partial}{\partial\beta}\left[\frac{e^{\beta uH(\cos\theta)}}{\beta uH}\right]\Bigg|_{(\cos\theta)=1}^{(\cos\theta)=-1}}{\left[\frac{e^{\beta uH(\cos\theta)}}{\beta uH}\right]\Bigg|_{(\cos\theta)=1}^{(\cos\theta)=-1}} \tag{1.34}$$

$$= N_0 u\frac{\frac{1}{uH}\frac{\partial}{\partial\beta}\left[\left(\frac{1}{\beta uH}\right)\left(e^{-\beta uH} - e^{\beta uH}\right)\right]}{\frac{1}{\beta uH}\left[e^{-\beta uH} - e^{\beta uH}\right]} \tag{1.35}$$

$$= N_0 u\frac{\left[\left(\frac{1}{\beta uH}\right)\frac{\partial}{\partial\beta}\left(e^{-\beta uH} - e^{\beta uH}\right) + \left(e^{-\beta uH} - e^{\beta uH}\right)\frac{\partial}{\partial\beta}\left(\frac{1}{\beta uH}\right)\right]}{\frac{1}{\beta}\left[e^{-\beta uH} - e^{\beta uH}\right]} \tag{1.36}$$

$$= N_0 u\frac{\left[\left(\frac{1}{\beta uH}\right)\left(-uHe^{-\beta uH} - uHe^{\beta uH}\right) + \left(e^{-\beta uH} - e^{\beta uH}\right)\left(\frac{-1}{\beta^2 uH}\right)\right]}{\frac{1}{\beta}\left[e^{-\beta uH} - e^{\beta uH}\right]} \tag{1.37}$$

$$= N_0 u\frac{\frac{1}{\beta uH}\left[\frac{1}{\beta}\left(e^{\beta uH} - e^{-\beta uH}\right) - uH\left(e^{-\beta uH} + e^{\beta uH}\right)\right]}{\frac{1}{\beta}\left[e^{-\beta uH} - e^{\beta uH}\right]} \tag{1.38}$$

$$= N_0 u \frac{\frac{1}{uH}\left[\frac{1}{\beta}\left(e^{\beta uH} - e^{-\beta uH}\right) - uH\left(e^{-\beta uH} + e^{\beta uH}\right)\right]}{-\left[e^{\beta uH} - e^{-\beta uH}\right]} \tag{1.39}$$

$$= N_0 u \frac{\frac{1}{uH\beta}\left[2\sinh(\beta uH) - 2uH\beta\cosh(\beta uH)\right]}{-2\sinh(\beta uH)} \tag{1.40}$$

$$= N_0 u \frac{1}{uH\beta}\left[-1 + uH\beta\coth(\beta uH)\right] \tag{1.41}$$

finalmente,

$$\bar{M}_z = N_0 u\left[\coth(uH/kT) - (kT/uH)\right] \tag{1.42}$$

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