Lista 3 - Termofísica II 18/03/21

1) A função partição Z,

$$Z = \int_{-\infty}^{\infty} e^{-E(p)\beta} \, d^3p$$

Sabendo $E(p) = cp$, onde c é a velocidade da luz no vácuo e p é o momento associado à partícula. Então, a função partição fica,

$$\boxed{\begin{aligned} PV &= nRT \\ &= Nk_BT \end{aligned}}$$

$\Delta x = \Delta y = \Delta z$

$\Delta p_x = \Delta p_y = \Delta p_z$

$$Z = \sum_{r,p} e^{-\beta E(x,p)}$$

$$= \frac{1}{(\Delta x \Delta p)^3} \iint e^{-\beta E} \, d^3r \, d^3p$$

$$= \frac{V}{h^3} \int e^{-\beta E} \, d^3p$$

vel. luz

$$= \frac{V}{h^3} \int_{-\infty}^{\infty} e^{-\beta cp} \, d^3p$$

$$= \frac{V}{h^3} \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} e^{-\beta c p} p^2 \operatorname{sen}\theta \, dp \, d\phi \, d\theta$$

$$= \frac{V}{h^3} 2\pi \int_0^{\pi} \operatorname{sen}\theta \, d\theta \int_0^{\infty} e^{-\beta c p} p^2 \, dp$$

$$= \frac{V}{h^3} 2\pi \left[-\cos\theta \Big|_0^{\pi} \right] \int_0^{\infty} p^2 e^{-\beta c p} \, dp$$

$$= \frac{V}{h^3} 2\pi \, 2 \int_0^{\infty} p^2 e^{-\beta c p} \, dp$$

$$= \frac{4\pi V}{h^3} \boxed{\int_0^{\infty} p^2 e^{-\beta c p} \, dp}$$

A integral em destaque é identificada como

$$I = \int_0^{\infty} p^2 e^{-\beta c p} \, dp$$

Utilizando a resolução por partes

$$uv - \int v\,du$$

$$I = \frac{p^2 e^{-\beta c p}}{-\beta c}\Bigg|_0^\infty - \int_0^\infty \frac{-1}{\beta c} e^{-\beta c p} 2p\,dp \qquad \begin{cases} u = p^2 \\ dv = e^{-\beta c p}\,dp \end{cases}$$

$$= \frac{-p^2}{\beta c} e^{-\beta c p}\Bigg|_0^\infty + \int_0^\infty \frac{2p}{\beta c} e^{-\beta c p}\,dp \qquad \begin{cases} du = 2p\,dp \\ v = \frac{-1}{\beta c} e^{-\beta c p} \end{cases}$$

$$\to 0$$

$$= \int_0^\infty \frac{2p}{\beta c} e^{-\beta c p}\,dp \qquad \begin{cases} u = p \\ dv = e^{-\beta c p}\,dv \end{cases}$$

$$= \frac{2}{\beta c}\left[\frac{-p}{\beta c} e^{-\beta c p}\Bigg|_0^\infty - \int_0^\infty \frac{-1}{\beta c} e^{-\beta c p}\,dp\right] \qquad \begin{cases} du = dp \\ v = \frac{-1}{\beta c} e^{-\beta c p} \end{cases}$$

$$\to 0$$

$$= \frac{2}{(\beta c)^2}\int_0^\infty e^{-\beta c p}\,dp = \frac{-2}{(\beta c)^3} e^{-\beta c p}\Bigg|_0^\infty$$

$$= \frac{2}{(\beta c)^3}$$

O que leva à função partição

$$Z = \frac{4\pi V}{(\hbar)^3}\int_0^{\infty} p^2 e^{-\beta c p}\, dp = \frac{4\pi V}{(\hbar)^3}\frac{2}{(\beta c)^3}$$

$$= \frac{8\pi V}{(\hbar\beta c)^3}$$

O que leva à energia U,

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

$$= (N) -\frac{\partial}{\partial\beta}\left[\ln(8\pi V) - 3\ln(\hbar\beta c)\right]$$

$$= (N) -\frac{\partial}{\partial\beta}\left[-3\ln(\hbar\beta c)\right]$$

$$= N\, 3\, \frac{1}{\hbar\beta c}\cdot \hbar c = 3 k_B T N$$

O calor específico C_V,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3k_B N$$

A entropia S,

$$S = k_B\left(\ln Z + \beta U\right)$$

$$= k_B\left(\ln(8\pi VN) - 3\ln(\hbar c\beta) + \beta \cdot 3k_B TN\right)$$

2) Considerando $E = c|q|$, c uma constante, a função partição fica,

$$Z = \frac{1}{(\Delta q)}\int_{-\infty}^{\infty} e^{-E\beta}\, dq$$

$$= \frac{1}{(\Delta q)}\int_{-\infty}^{\infty} e^{-c|q|\beta}\, dq$$

Devido ao módulo a função partição é definida,

$$Z = \begin{cases} \dfrac{1}{(\Delta q)} \displaystyle\int_{-\infty}^{\infty} e^{-c\beta q}\, dq \,, & q > 0 \\ \dfrac{1}{(\Delta q)} \displaystyle\int_{-\infty}^{\infty} e^{+c\beta q}\, dq \,, & q \leq 0 \end{cases}$$

Tomando,

$$I_{>} = \int_{0}^{\infty} e^{-c\beta q}\, dq$$

$$I_{<} = \int_{-\infty}^{0} e^{c\beta q}\, dq$$

Agora resolvendo $I_{>}$,

$$I_{>} = \left[\frac{-1}{c\beta} e^{-c\beta q} \right] \Bigg|_{0}^{+\infty} = \frac{-1}{c\beta} \left[0 - 1 \right] = \frac{1}{\beta c}$$

$I_<$ fica,

$$I_< = \int_{-\infty}^{0} e^{c\beta q} dq = \frac{1}{c\beta}\left[e^{c\beta q} \right]\Big|_{-\infty}^{0}$$

$$= \frac{1}{\beta c}$$

Assim, a energia média $\bar{E}$

$$\bar{E} = -\frac{\partial}{\partial\beta}(\ln Z) = -\frac{\partial}{\partial\beta}\left[\ln\left(\frac{1}{\beta c}\right)\right]$$

$$= \frac{\partial}{\partial\beta}(\ln\beta c) = \frac{1}{\beta c}\, c = k_B T$$

3) A posição média $\bar{x}$ é escrita por

$$\bar{x} = \int x\, P(x)\, dx$$

onde $p(x)$ é a probabilidade de se

encontrar a partícula. A probabilidade $P(x)$ é dada por

$$P(x) = \frac{e^{-\beta u(x)}}{\int e^{-\beta u(x)} dx}$$

O que nos leva a,

$$\bar{x} = \frac{\int x e^{-\beta u(x)} dx}{\int e^{-\beta u(x)} dx}$$

b) Como o potencial $u(x)$ tem um mínimo em x_0, implicando que

$$\left.\frac{du(x)}{dx}\right|_{x_0} = 0$$

Isso faz com que a expansão em série do potencial tenha em torno da posição de equilíbrio seja

$$u(x) = u(x_0) + (x - x_0)\cancel{\left.\frac{du(x)}{dx}\right|_{x_0}} + (x-x_0)^2 \left.\frac{d^2u}{dx^2}\right|_{x_0} + \cdots$$

$$= u(x_0) + (x-x_0)^2 \frac{d^2u}{dx^2}\bigg|_{x_0} + \cdots$$

Truncando a série até a derivada de 2ª ordem,

$$u(x) = u(x_0) + \frac{(x-x_0)^2}{2} \frac{d^2u}{dx^2}\bigg|_{x_0}$$

$\rightarrow \Gamma = \text{const.}$

Isso leva à integral,

$$\int x\, e^{-\beta\left(u(x_0) + (x-x_0)^2 \Gamma\right)} dx$$

$$e^{-\beta u(x_0)} \int x\, e^{-(x-x_0)^2 \Gamma \beta} dx$$

Fazendo $u = x - x_0$

$$e^{-\beta u(x_0)} \int (u+x_0)\, e^{-u^2 \Gamma \beta} du$$

$$e^{-\beta u(x_0)} \left[\int \cancelto{0}{u\, e^{-u^2 \Gamma \beta}} du + x_0 \int e^{-u^2 \Gamma \beta} du \right]$$

$$x_0 e^{-\beta u(x_0)} \int e^{-u^2 \Gamma \beta} du$$

Assim, $\bar{x}$ fica

$$\bar{x} = \frac{x_0 e^{-\beta u(x_0)} \int e^{-u^2 \Gamma \beta} du}{e^{-\beta u(x_0)} \int e^{-u^2 \Gamma \beta} du}$$

$$\bar{x} = x_0 \cancel{\int}$$

c) O termo cúbico de $u(x)$

$$u(x) = u(x_0) + \Gamma (x - x_0)^2 + \gamma (x - x_0)^3$$

A integral fica,

$$\int e^{-\beta\left(u(x_0) + \Gamma (x-x_0)^2 + \gamma (x-x_0)^3\right)} dx$$

$$e^{-\beta u(x_0)} \int e^{-\beta\left(\Gamma (x-x_0)^2 + \gamma (x-x_0)^3\right)} dx$$

Expandindo a exponencial do termo cúbico,

$$e^{-\beta u(x_0)} \int e^{-\beta\Gamma(x-x_0)^2} \left[1 - \beta\gamma(x-x_0)^3 \right] dx$$

Fazendo $u = (x - x_0)$, $\bar{x}$ fica

$$\bar{x} = \frac{\int x\, e^{-u(x)\beta}\, dx}{\int e^{-u(x)\beta}}$$

$$= \frac{\cancel{e^{-\beta u(x_0)}} \int (u+x_0)\, e^{-\beta\Gamma u^2} \left[1 + \beta\gamma u^3 \right] du}{\cancel{e^{-\beta u(x_0)}} \int e^{-\beta\Gamma u^2} \left[1 + \beta\gamma u^3 \right] du}$$

$$= \frac{\int (u+x_0)\, e^{-\beta\Gamma u^2} \left[1 + \beta\gamma u^3 \right] du}{\int e^{-\beta\Gamma u^2} \left[1 + \beta\gamma u^3 \right] du} = \frac{\int (x_0 + \beta\gamma u^4)\, e^{-\beta\Gamma u^2}\, du}{\int e^{-\beta\Gamma u^2}\, du}$$

$$\sqrt{\frac{\pi}{\beta\Gamma}}$$

Usando a propriedade $I(\alpha) = \sqrt{\frac{\pi}{\alpha}}$,

$$\frac{3}{4\beta^2\Gamma^2}\sqrt{\frac{\pi}{\beta\Gamma}}$$

$$\bar{x} = x_0\sqrt{\frac{\pi}{\beta\Gamma}} + \beta\gamma\int u^4 e^{-\beta\Gamma u^2}\,du$$

$$\sqrt{\frac{\pi}{\beta\Gamma}}$$

$$= x_0 + \beta\gamma\,\frac{3}{4\beta^2\Gamma^2} = x_0 + \frac{3\gamma}{4\beta\Gamma^2}$$

d) O potencial Lennard-Jones $u(x)$,

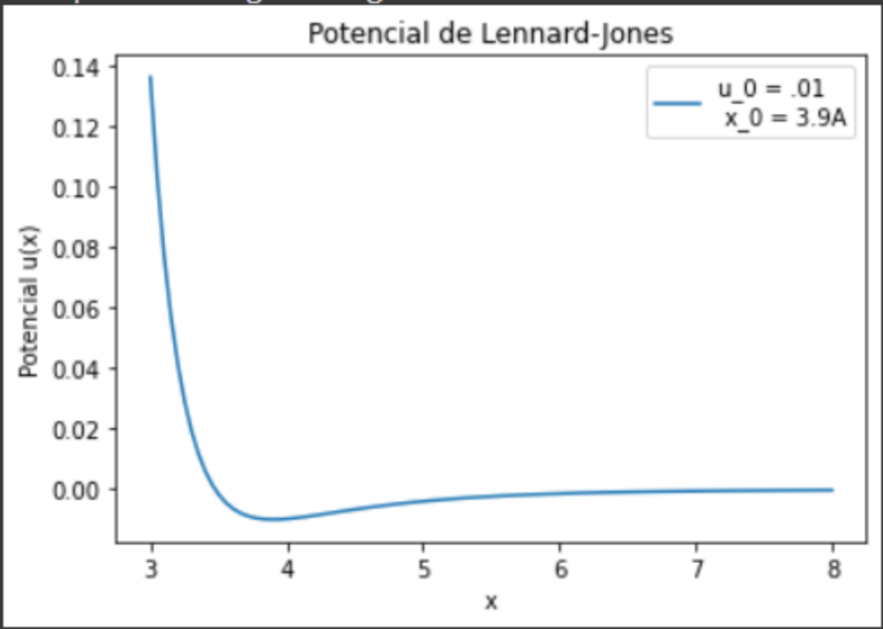
$$u(x) = u_0\left[\left(\frac{x_0}{x}\right)^{12} - 2\left(\frac{x_0}{x}\right)^{6}\right]$$

```python
plt.xlabel("x")
plt.ylabel("Potencial u(x)")

# Constantes
x_0 = 3.9
u_0 = .010
x = np.linspace(3.,8.,100)

y = u_0*(x_0/x)**12 - 2*u_0*(x_0/x)**6
plt.plot(x,y, label = "u_0 = .01 \n x_0 = 3.9A" )
plt.legend()
```

```
<matplotlib.legend.Legend at 0x7fbdfb89e4d0>
```



Expandindo o potencial de Lennard-Jones em Série de Taylor em torno de x_0,

$$u(x) = u_0 + (x-x_0)\left.\frac{du}{dx}\right|_{x_0} + \frac{(x-x_0)^2}{2!}\left.\frac{d^2u}{dx^2}\right|_{x_0} + \cdots$$

Calculando as derivadas,

$$\left.\frac{du(x)}{dx}\right|_{x_0} = 0 \quad \Big\{ \text{Por haver um mínimo}$$

$$\left.\frac{d\,u(x)}{dx}\right|_{x_0} = \frac{u_0(-12)\,x_0^{12}}{x^{13}} - \frac{2u_0(-6)\,x_0^{6}}{x^{7}} = 0$$

A 2ª derivada,

$$\left.\frac{d^2u(x)}{dx^2}\right|_{x_0} = \left.\frac{u_0(-12)(-13)\,x_0^{12}}{x^{14}}\right|_{x_0} - \left.\frac{2(-6)(-7)\,u_0\,x_0^{6}}{x^{8}}\right|_{x_0}$$

$$= \frac{u_0\overbrace{(12\cdot13)}^{156}}{x_0^2} - \frac{\overbrace{2\cdot7\cdot6}^{84}\,u_0}{x_0^2}$$

$$= \frac{72\,u_0}{x_0^2}$$

A 3ª derivada,

$$\left.\frac{d^3u(x)}{dx^3}\right|_{x_0} = \left.\frac{u_0(-12\cdot13\cdot14)\,x_0^{12}}{x^{15}}\right|_{x_0} + \left.\frac{2(6\cdot7\cdot8)\,u_0\,x_0^{6}}{x^{9}}\right|_{x_0}$$

$$= \frac{-2184}{x_0^3}u_0 + \frac{672}{x_0^3}u_0 = \frac{-1512\,u_0}{x_0^3}$$

Os termos obtidos na letra c

$$\Gamma = \frac{1}{2}\frac{d^2u}{dx^2} = \frac{36u_0}{x_0^2}$$

$$\gamma = \frac{1}{6}\frac{d^3u}{dx^3} = \frac{-252u_0}{x_0^3}$$

Assim, o coeficiente de expansão térmica fica,

$$\alpha = \frac{-3}{4}\frac{\gamma}{\beta\Gamma^2}\frac{1}{x_0}$$

$$= \frac{-3}{4\beta x_0}\left(\frac{-252u_0}{x_0^3}\right)\left(\frac{x_0^2}{36u_0}\right)^2$$

Para o argônio o valor calculado é

$$\alpha \simeq 0{,}0013\ K^{-1}$$

O valor medido é $0{,}0007\ K^{-1}$, cerca do dobro do calculado.

4) O valor mais provável tem a condição de

$$\frac{dF(v)}{dv} = 0$$

Onde $F(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{\frac{-mv^2}{2k_B T}}$. Tomando

$C = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2}$ calculamos dF/dv como

$$\left.\frac{dF}{dv}\right|_{\tilde{v}} = \frac{d}{dv}\left(C v^2 e^{-\frac{m}{2}v^2\beta} \right)\Bigg|_{\tilde{v}}$$

$$= 2C\tilde{v} e^{-\frac{m}{2}v^2\beta} + C\tilde{v}^2(-m\beta)2\tilde{v} e^{-\frac{m}{2}\tilde{v}^2\beta}$$

Isolando $\tilde{v}$,

$$\cancel{2}\cancel{C}\cancel{\tilde{v}}\cancel{e^{-\frac{m}{2}\tilde{v}^2\beta}} = \cancel{C}\tilde{v}^2\left(\frac{m}{2}\beta\right)\cancel{2\tilde{v}}\cancel{e^{-\frac{m}{2}\tilde{v}^2\beta}}$$

$$2 = \tilde{v}^2(m\beta)$$

$$\boxed{\tilde{v} = \sqrt{\frac{2k_B T}{m}}}$$

5) A velocidade média $\bar{v}$ é

$$\bar{v} = \int_0^\infty F(v)\, v\, dv$$

$$= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \boxed{\int_0^\infty e^{\frac{-mv^2}{2kT}} v^3 dv}$$

Resolvendo a integral em destaque via integração por partes,

$$= \cancel{v^3 e^{\frac{-mv^2}{2k_BT}}\Big|_0^\infty} \rightarrow 0 - \int_0^\infty e^{\frac{-mv^2}{2k_BT}} 3v^2 dv$$

$u = v^3$

$dv = e^{-\alpha v^2} dv$

$du = 3v^2$

$v =$

$uv - \int v\, du$

$$-3\int_0^\infty e^{\frac{-mv^2}{2k_BT}} v^2 dv$$

Como identifica-se a integral como uma integral gaussiana diferenciando em relação a α,

$$\bar{v} = 3 \cdot \frac{4\pi}{2} \left(\frac{m\beta}{2\pi}\right)^{3/2} \left(\frac{\alpha}{\beta m}\right)^2 = \sqrt{\frac{8kT}{\pi m}}$$

6) O valor médio de v^2 é dado por,

$$\overline{v^2} = \int_0^\infty F(v)\, v^2\, dv$$

$$= 4\pi \left(\frac{m\beta}{2\pi} \right)^{3/2} \int_0^\infty e^{\frac{-mv^2}{2k_BT}}\, v^4\, dv$$

Assim como na questão passa utilizaremos $I(\alpha)$ diferenciando 2 vezes em relação a α,

$$\frac{d^2\, I(\alpha)}{d\alpha^2} = \frac{3}{4\alpha^2}\sqrt{\frac{\pi}{\alpha}}$$

Tomando $\alpha = \frac{m\beta}{2}$, $\overline{v^2}$ fica,

$$\overline{v^2} = 4\pi \left(\frac{m\beta}{2\pi} \right)^{3/2} \frac{3 \cdot 4}{4\, m^2\beta^2} \sqrt{\frac{2\pi}{m\beta}} = \boxed{\frac{3}{m\beta}}$$

7) A distribuição de velocidade para $T = 300K$ e para até $300 m/s$,

$$\int_0^{300} F(v)\,dv = \left(\frac{m\beta}{2\pi}\right)^{3/2} 4\pi \int_0^{300} v^2 e^{-\frac{m v^2 \beta}{2}}\,dv$$

Fazendo $u = v\sqrt{\frac{m\beta}{2}}$, $m = (28) \cdot 1{,}66 \times 10^{-27}$ kg

$$\int_0^{300\sqrt{\frac{m\beta}{2}} \simeq 0{,}71} u^2 e^{-u^2} = \quad \%$$

Obs: integrar numericamente
Google Colab

8) Diferentemente do caso 3D, no caso 2D $F(v) \approx 2\pi v$ ao invés de $4\pi v^2$

$$F(v) = C\,(2\pi v)\,e^{-\frac{m\beta v^2}{2}}$$

Normalizando $\quad u = \frac{1}{\sqrt{\frac{m\beta}{2}}}\,v$

$$1 = \int_0^\infty 2\pi C\, v\, e^{-\frac{m\beta v^2}{2}}\, dv = 2\pi C \int_0^\infty v\, e^{-\frac{m\beta v^2}{2}}\, dv$$

Fazendo $u = \frac{1}{\sqrt{\frac{m\beta}{2}}}\,v$,

$$1 = 2\pi C \int_0^\infty \left(\frac{2}{m\beta}\right) u\, e^{-u^2}\, du$$

$$1 = 2\pi C\, \frac{2}{m\beta}\, \frac{1}{2}$$

$$C = \frac{m\beta}{2}$$

Assim,

$$F(v) = \left(\frac{m\beta}{2\pi}\right) 2\pi v\, e^{-\frac{m v^2 \beta}{2}}$$

A velocidade mais provável $\tilde{v}$,

$$\left.\frac{dF}{dv}\right|_{\tilde{v}} = 0$$

$$= \left(\frac{m\beta}{\cancel{2\pi}}\right)\cancel{2\pi}\, e^{-\frac{m\tilde{v}^2\beta}{2}}$$

$$+ \left(\frac{m\beta}{\cancel{2\pi}}\right)\cancel{2\pi}\,\tilde{v}\left(\frac{-m\beta}{\cancel{2}}\right)\cancel{2}\tilde{v}\, e^{-\frac{m\beta\tilde{v}^2}{2}}$$

$$= m\beta\left(1 - \tilde{v}^2 m\beta\right) e^{-\frac{m\beta\tilde{v}^2}{2}}$$

O termo em parenteses deve ser 0,

$$\tilde{v} = \sqrt{\frac{1}{m\beta}}$$