O ensemble grande canônico – 2

Alexandre Diehl

Departamento de Física – UFPel

Flutuação na energia

$$\sigma_E^2 \equiv \langle(\Delta E^2\rangle = \langle(E-\langle E\rangle)^2\rangle = \langle E^2\rangle - \langle E\rangle^2 \quad\rightarrow\quad \begin{cases} \langle E\rangle = -\left(\dfrac{\partial \ln \Xi}{\partial\beta}\right)_{z,V} = -\dfrac{1}{\Xi}\left(\dfrac{\partial \Xi}{\partial\beta}\right)_{z,V} \\ \langle E\rangle = -\left(\dfrac{\partial \ln \Xi}{\partial\beta}\right)_{\mu,V} + \mu\langle N\rangle \end{cases}$$

Usando a grande função de partição como $\Xi = \Xi(z, V, \beta)$:

$$\langle E^2\rangle = \frac{1}{\Xi}\sum_i E_i^2\, e^{-\beta E_i} z^{N_i} = \frac{1}{\Xi}\frac{\partial^2}{\partial\beta^2}\left[\sum_i e^{-\beta E_i} z^{N_i}\right]_{z,V} = \frac{1}{\Xi}\left(\frac{\partial^2 \Xi}{\partial\beta^2}\right)_{z,V}$$

$$\sigma_E^2 = \frac{1}{\Xi}\left(\frac{\partial^2\Xi}{\partial\beta^2}\right)_{z,V} - \frac{1}{\Xi^2}\left(\frac{\partial\Xi}{\partial\beta}\right)^2_{z,V} = \frac{\partial}{\partial\beta}\left(\frac{1}{\Xi}\frac{\partial\Xi}{\partial\beta}\right)_{z,V} = \frac{\partial}{\partial\beta}\left(\frac{\partial\ln\Xi}{\partial\beta}\right)_{z,V} = \left(\frac{\partial^2\ln\Xi}{\partial\beta^2}\right)_{z,V}$$

$$\sigma_E^2 = \frac{\partial}{\partial\beta}\left(\frac{\partial\ln\Xi}{\partial\beta}\right)_{z,V} = -\left(\frac{\partial\langle E\rangle}{\partial\beta}\right)_{z,V} \quad\rightarrow\quad \boxed{\sigma_E^2 = k_B T^2\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{z,V}}$$

Flutuação na energia

$$\sigma_E^2 = k_B T^2 \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{z,V} \quad \rightarrow$$

Como relacionar σ_E^2 com alguma propriedade física?

Escrevemos $E = E(T, V, N) = E(T, V, N(z, V, T))$

$$\left(\frac{\partial \langle E \rangle}{\partial T}\right)_{z,V} = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{V,N} + \left(\frac{\partial \langle E \rangle}{\partial N}\right)_{T,V} \left(\frac{\partial N}{\partial T}\right)_{z,V}$$

- Capacidade térmica C_V
- Contribuição extra às flutuações na energia, devido à variação de N
- O último termo pode ser expresso em termos de $\langle E \rangle$

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Flutuação no número de partículas

$$\sigma_E^2 = k_B T^2 \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{z,V} \quad \rightarrow$$ Como relacionar σ_E^2 com alguma propriedade física?

Outra forma de reduzir a derivada de interesse: usando **transformações Jacobianas**

$$\begin{aligned}
\left(\frac{\partial \langle E \rangle}{\partial T}\right)_{z,V} &= \frac{\partial(\langle E \rangle, z, V)}{\partial(T,z,V)} = \frac{\partial(\langle E \rangle, z, V)}{\partial(T,N,V)} \frac{\partial(T,N,V)}{\partial(T,z,V)} \\
&= \det \begin{pmatrix} \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} & \left(\frac{\partial \langle E \rangle}{\partial N}\right)_{T,V} & \left(\frac{\partial \langle E \rangle}{\partial V}\right)_{T,N} \\ \left(\frac{\partial z}{\partial T}\right)_{N,V} & \left(\frac{\partial z}{\partial N}\right)_{T,V} & \left(\frac{\partial z}{\partial V}\right)_{T,N} \\ \left(\frac{\partial V}{\partial T}\right)_{N,V} & \left(\frac{\partial V}{\partial N}\right)_{T,V} & \left(\frac{\partial V}{\partial V}\right)_{T,N} \end{pmatrix} \det \begin{pmatrix} \left(\frac{\partial T}{\partial T}\right)_{z,V} & \left(\frac{\partial T}{\partial z}\right)_{T,V} & \left(\frac{\partial T}{\partial V}\right)_{T,z} \\ \left(\frac{\partial N}{\partial T}\right)_{z,V} & \left(\frac{\partial N}{\partial z}\right)_{T,V} & \left(\frac{\partial N}{\partial V}\right)_{T,z} \\ \left(\frac{\partial V}{\partial T}\right)_{z,V} & \left(\frac{\partial V}{\partial z}\right)_{T,V} & \left(\frac{\partial V}{\partial V}\right)_{T,z} \end{pmatrix} \\
&= \det \begin{pmatrix} \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} & \left(\frac{\partial \langle E \rangle}{\partial N}\right)_{T,V} & \left(\frac{\partial \langle E \rangle}{\partial V}\right)_{T,N} \\ \left(\frac{\partial z}{\partial T}\right)_{N,V} & \left(\frac{\partial z}{\partial N}\right)_{T,V} & \left(\frac{\partial z}{\partial V}\right)_{T,N} \\ 0 & 0 & 1 \end{pmatrix} \det \begin{pmatrix} 1 & 0 & 0 \\ \left(\frac{\partial N}{\partial T}\right)_{z,V} & \left(\frac{\partial N}{\partial z}\right)_{T,V} & \left(\frac{\partial N}{\partial V}\right)_{T,z} \\ 0 & 0 & 1 \end{pmatrix} \\
&= \left[\left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} \left(\frac{\partial z}{\partial N}\right)_{T,V} - \left(\frac{\partial z}{\partial T}\right)_{N,V} \left(\frac{\partial \langle E \rangle}{\partial N}\right)_{T,V}\right] \left[\left(\frac{\partial N}{\partial z}\right)_{T,V}\right]
\end{aligned}$$

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&= \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} \underbrace{\left(\frac{\partial z}{\partial N}\right)_{T,V} \left(\frac{\partial N}{\partial z}\right)_{T,V}}_{=1} - \left(\frac{\partial z}{\partial T}\right)_{N,V} \left(\frac{\partial \langle E \rangle}{\partial N}\right)_{T,V} \left(\frac{\partial N}{\partial z}\right)_{T,V}
\end{aligned}$$

Flutuação no número de partículas

$$\sigma_E^2 = k_B T^2 \left(\frac{\partial \langle E\rangle}{\partial T}\right)_{z,V} \quad \rightarrow \quad \text{Como relacionar } \sigma_E^2 \text{ com alguma propriedade física?}$$

Outra forma de reduzir a derivada de interesse: usando **transformações Jacobianas**

$$\left(\frac{\partial \langle E\rangle}{\partial T}\right)_{z,V} = \frac{\partial(\langle E\rangle, z, V)}{\partial(T,z,V)} = \frac{\partial(\langle E\rangle, z, V)}{\partial(T,N,V)}\frac{\partial(T,N,V)}{\partial(T,z,V)}$$

$$= \det\begin{pmatrix} \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{N,V} & \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V} & \left(\frac{\partial\langle E\rangle}{\partial V}\right)_{T,N} \\ \left(\frac{\partial z}{\partial T}\right)_{N,V} & \left(\frac{\partial z}{\partial N}\right)_{T,V} & \left(\frac{\partial z}{\partial V}\right)_{T,N} \\ \left(\frac{\partial V}{\partial T}\right)_{N,V} & \left(\frac{\partial V}{\partial N}\right)_{T,V} & \left(\frac{\partial V}{\partial V}\right)_{T,N} \end{pmatrix} \det\begin{pmatrix} \left(\frac{\partial T}{\partial T}\right)_{z,V} & \left(\frac{\partial T}{\partial z}\right)_{T,V} & \left(\frac{\partial T}{\partial V}\right)_{T,z} \\ \left(\frac{\partial N}{\partial T}\right)_{z,V} & \left(\frac{\partial N}{\partial z}\right)_{T,V} & \left(\frac{\partial N}{\partial V}\right)_{T,z} \\ \left(\frac{\partial V}{\partial T}\right)_{z,V} & \left(\frac{\partial V}{\partial z}\right)_{T,V} & \left(\frac{\partial V}{\partial V}\right)_{T,z} \end{pmatrix}$$

$$= \det\begin{pmatrix} \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{N,V} & \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V} & \left(\frac{\partial\langle E\rangle}{\partial V}\right)_{T,N} \\ \left(\frac{\partial z}{\partial T}\right)_{N,V} & \left(\frac{\partial z}{\partial N}\right)_{T,V} & \left(\frac{\partial z}{\partial V}\right)_{T,N} \\ 0 & 0 & 1 \end{pmatrix} \det\begin{pmatrix} 1 & 0 & 0 \\ \left(\frac{\partial N}{\partial T}\right)_{z,V} & \left(\frac{\partial N}{\partial z}\right)_{T,V} & \left(\frac{\partial N}{\partial V}\right)_{T,z} \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{N,V} + \left(\frac{\partial z}{\partial T}\right)_{N,V}\left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\frac{\left(\frac{\partial T}{\partial z}\right)_{N,V}}{\left(\frac{\partial T}{\partial N}\right)_{z,V}}$$

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$$\sigma_E^2 = k_B T^2 \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{z,V} \quad \rightarrow$$

Como relacionar σ_E^2 com alguma propriedade física?

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&= \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{N,V} + \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\left(\frac{\partial N}{\partial T}\right)_{z,V}
\end{aligned}$$

Flutuação no número de partículas

$$\left(\frac{\partial N}{\partial T}\right)_{z,V} = -\frac{1}{k_B T^2}\left(\frac{\partial \langle N\rangle}{\partial \beta}\right)_{z,V}$$

onde usamos $\langle N\rangle = N$, válido no limite termodinâmico

Como $\langle N\rangle = z\left(\frac{\partial \ln \Xi}{\partial z}\right)_{T,V}$

$$\left(\frac{\partial N}{\partial T}\right)_{z,V} = -\frac{1}{k_B T^2}\left(\frac{\partial}{\partial \beta}\left\{z\left(\frac{\partial \ln \Xi}{\partial z}\right)_{T,V}\right\}\right)_{z,V} = -\frac{1}{k_B T^2}\left(z\left(\frac{\partial^2 \ln \Xi}{\partial \beta \partial z}\right)_{T,V}\right)_{z,V}$$

$$= -\frac{1}{k_B T^2}\left(z\left(\frac{\partial^2 \ln \Xi}{\partial z \partial \beta}\right)_{T,V}\right)_{z,V} = -\frac{1}{k_B T^2}\left(z\frac{\partial}{\partial z}\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{z,V}\right)_{T,V}$$

Como $\langle E\rangle = -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{z,V}$ e $z = e^{\beta\mu}$

$$\left(\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{k_B T^2}\left(z\frac{\partial \langle E\rangle}{\partial z}\right)_{T,V} \rightarrow \boxed{\left(\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{T}\left(\frac{\partial \langle E\rangle}{\partial \mu}\right)_{T,V}}$$

Flutuação no número de partículas

$$\left(\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{T}\left(\frac{\partial\langle E\rangle}{\partial\mu}\right)_{T,V} = \frac{1}{T}\left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V}$$

Como $\sigma_N^2 = \frac{1}{\beta}\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V}$ é a flutuação em N $\rightarrow$ $\boxed{\left(\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{T}\left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\beta\,\sigma_N^2}$

Assim, a **flutuação em energia** se escreve como

$$\begin{aligned}
\sigma_E^2 = k_B T^2\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{z,V} &= k_B T^2\left[\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{V,N} + \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\left(\frac{\partial N}{\partial T}\right)_{z,V}\right] \\
&= k_B T^2\left[C_V + \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\frac{1}{T}\left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\beta\,\sigma_N^2\right] \\
&= k_B T^2\left[C_V + \frac{1}{k_B T^2}\left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}^2\sigma_N^2\right]
\end{aligned}$$

$$\boxed{\sigma_E^2 = k_B T^2 C_V + \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}^2\sigma_N^2}$$

Flutuação no número de partículas

$$\sigma_E^2 = k_B T^2 C_V + \left(\frac{\partial\langle E\rangle}{\partial N}\right)^2_{T,V} \sigma_N^2$$

- Contribuição canônica às flutuações

Comportamento da flutuação em energia no limite termodinâmico

$$C_V \sim N \qquad \sigma_N^2 \sim N \qquad \langle E\rangle \sim N \quad \rightarrow \quad \frac{\partial\langle E\rangle}{\partial N} \sim \frac{N}{N} \sim 1 \qquad \rightarrow \qquad \sigma_E^2 \sim N$$

Com isto, o **desvio relativo** em E se comporta como

$$\frac{\sigma_E}{\langle E\rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \rightarrow 0 \qquad \text{quando} \quad N \rightarrow \infty$$

As flutuações em energia e número de partículas se anulam no limite termodinâmico:

no ensemble grande canônico, a maior parte dos microestados acessíveis ao sistema é encontrado em torno de seus valores médios.