Notes of JU Guoxing TD&SP

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1 Introduction

热力学量：formal additivity (形式可加性) + 均匀性
与物质量(m,n,N)的关系：
extensive quantity (广延量)
intensive quantity (强度量)
与过程的关系：
过程量 $\mathrm{d}W$, $-p\mathrm{d}V$, $\mathrm{d}Q$, $T\mathrm{d}S$
状态量

2 Heat

2.2 Heat Capacity

def:

$$C = \frac{\mathrm{d}Q}{\mathrm{d}T} \tag{2.2.1}$$

Heat capacity is a kind of response function (响应函数，体现系统对外界作用的响应情况).
与过程有关.

Other response fxn involving state fxn ($f(T, V, p) = 0,\ V = V(T, p),\ p = p(T, V)$)
1) isobaric expansivity (定压膨胀系数)

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{2.2.2}$$

2) isochoric pressure coefficient
3) isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{2.2.3}$$

and there exists a connection between them

$$\alpha = \kappa_T \beta p \tag{2.2.4}$$

e.g.

Homework

1.3, 1.5, 2.2, 2.5

Proof

For $f(x, y, z) = 0$

(i)

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{2.2.5}$$

(ii)

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \tag{2.2.6}$$

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Heat capacity per mass unit (specific heat capacity)

$$c = \frac{1}{m}\frac{\mathrm{d}Q}{\mathrm{d}T} \tag{2.2.7}$$

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \tag{2.2.8}$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p \tag{2.2.9}$$

3 Probability

3.4 variance

def: variance

$$\sigma_x^2 = \langle (x - \langle x \rangle)^2 \rangle \tag{3.4.1}$$

standard deviation

$$\sigma_x = \sqrt{\langle (x - \langle x \rangle)^2 \rangle} \tag{3.4.2}$$

Discussion: 1)

$$\begin{aligned} \sigma_x^2 &= \langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle \\ &= \langle x^2 \rangle - \langle x \rangle^2 \end{aligned} \tag{3.4.3}$$

2) k-degree moment: $\langle (x - \langle x \rangle)^k \rangle$
k=1 average deviation
k=2 variance
k=3 skewness(偏斜度)
k=4 kurtosis(峭度)

3.5 Linear Transform and Variance

suppose

$$y = ax + b \tag{3.5.1}$$

where a and b are constants
we have

$$\langle y \rangle = a\langle x \rangle + b \tag{3.5.2}$$

thus

$$\langle y^2 \rangle = \langle a^2x^2 + 2abx + b^2 \rangle = a^2\langle x^2 \rangle + 2ab\langle x \rangle + b^2 \tag{3.5.3}$$

$$\langle y \rangle^2 = a^2\langle x \rangle^2 + 2ab\langle x \rangle + b^2 \tag{3.5.4}$$

$$\sigma_y^2 = a^2\langle x^2 \rangle - a^2\langle x \rangle^2 = a^2\sigma_x^2 \tag{3.5.5}$$

$$\sigma_y = a\sigma_x \tag{3.5.6}$$

3.6 independent variable

Suppose u and v are independent random variables, the probability of $u \sim u + \mathrm{d}u$ and $v \sim v + \mathrm{d}v$ is

$$P_u(u)\,\mathrm{d}u\,P_v(v)\,\mathrm{d}v \tag{3.6.1}$$

$$\begin{aligned} \langle uv \rangle &= \iint uvP_u(u)P_v(v)\,\mathrm{d}u\,\mathrm{d}v \\ &= \int uP_u(u)\,\mathrm{d}u \int vP_v(v)\,\mathrm{d}v \\ &= \langle u \rangle \langle v \rangle \end{aligned} \tag{3.6.2}$$

Suppose we have n independent random variables X_i, all with average $\langle X \rangle$ and variance σ_X^2, and $Y = X_1 + \cdots + X_n$, show the average and variance of Y.

$$\langle Y \rangle = n\langle X \rangle \tag{3.6.3}$$

$$\sigma_Y^2 = \langle Y^2 \rangle - \langle Y \rangle^2 \tag{3.6.4}$$

where

$$\begin{aligned}\langle Y^2\rangle &= \langle X_1^2 + \cdots + X_n^2 + 2X_1X_2 + \cdots\rangle \\ &= n\langle X^2\rangle + n(n-1)\langle X\rangle^2\end{aligned} \tag{3.6.5}$$

thus

$$\sigma_Y^2 = n\langle X^2\rangle - n\langle X\rangle^2 = n\sigma_X^2 \tag{3.6.6}$$

$$\sigma_Y = \sqrt{n}\sigma_X \tag{3.6.7}$$

which means, suppose $average(x) = \dfrac{\sum_{\mathrm{i=1}}^{\mathrm{n}} X_i}{n}$

$$\sigma_{average(x)} = \frac{\sqrt{n}\sigma_X}{n} = \frac{\sigma_X}{\sqrt{n}} \tag{3.6.8}$$

3.7 Binomial Distribution

Bernoulli Trial

$$P(x) = \begin{cases} p & \text{"}success\text{"} \\ 1-p & \text{"}fail\text{"} \end{cases} \tag{3.7.1}$$

Binomial Distribution

prob of k successes in n independent trials:

$$P(n,k) = C_n^k p^k (1-p)^{n-k} \tag{3.7.2}$$

$$\langle k\rangle = np \tag{3.7.3}$$

$$\sigma_k^2 = np(1-p) \tag{3.7.4}$$

fractional width (相对宽度) of the distribution:

$$\frac{\sigma_k}{\langle k\rangle} = \sqrt{\frac{1-p}{np}} \propto \frac{1}{\sqrt{n}} \tag{3.7.5}$$

Poisson Distribution

Exponential Distribution

Moment Generating Function