

Solutions to homework assignment 2

1.1 (i) $P(x) = \frac{1}{\sqrt{2\pi}} \frac{1}{\sigma} e^{-\frac{(x-\bar{x})^2}{2\sigma^2}}$ Use $\int_{-\infty}^{\infty} e^{-\lambda x^2} = \sqrt{\frac{\pi}{\lambda}}$

$$\int_{-\infty}^{\infty} dx P(x) = \frac{1}{\sqrt{2\pi}} \frac{1}{\sigma} \sqrt{2\pi\sigma^2} = 1$$

$$\int_{-\infty}^{\infty} x dx P(x) = \frac{1}{\sqrt{2\pi}} \frac{1}{\sigma} \int_{-\infty}^{\infty} e^{-\frac{(x-\bar{x})^2}{2\sigma^2}} x dx \quad y = x - \bar{x}$$

$$= \frac{1}{\sqrt{2\pi}} \frac{1}{\sigma} \int_{-\infty}^{\infty} e^{-\frac{y^2}{2\sigma^2}} (\bar{x} + y) dy = \bar{x}$$

↓
odd, so $\rightarrow 0$

$$\langle \Delta x \rangle_{\text{rms}} = \left[\int_{-\infty}^{\infty} (x-\bar{x})^2 P(x) dx \right]^{\frac{1}{2}} = \left[\frac{1}{\sqrt{2\pi}} \frac{1}{\sigma} \left(-\frac{2}{\partial \lambda} \right) \int_{-\infty}^{\infty} e^{-\lambda(x-\bar{x})^2} dx \right]^{\frac{1}{2}}$$

$\sqrt{\pi} (-1/2) \lambda^{-\frac{3}{2}}$
 $\sqrt{\frac{\pi}{\lambda}}$
 $\lambda = \frac{1}{2\sigma^2}$

$$= \left(\frac{1}{\sqrt{2\pi}} \frac{1}{\sigma} \frac{\sqrt{\pi}}{2} (2\sigma^2) \right)^{\frac{1}{2}} = \left[\sigma^2 \right]^{\frac{1}{2}} = \sigma$$

(ii) $\frac{1}{\sigma^2} = \frac{1}{kT_1^2 C_{v1}} + \frac{1}{kT_2^2 C_{v2}}$

For ideal gases, $C_{vi} = \frac{3}{2} N_i k$, so

$$\frac{1}{\sigma^2} = \frac{1}{\frac{3}{2} N_1 k T_1^2} + \frac{1}{\frac{3}{2} N_2 k T_2^2}$$

1.1. (a) We expand the quantity $\ln \Omega^{(0)}(E_1)$ as a Taylor series in the variable $(E_1 - \bar{E}_1)$ and get

$$\begin{aligned} \ln \Omega^{(0)}(E_1) &\equiv \ln \Omega_1(E_1) + \ln \Omega_2(E_2) & (E_2 = E^{(0)} - E_1) \\ &= \{ \ln \Omega_1(\bar{E}_1) + \ln \Omega_2(\bar{E}_2) \} + \\ &\quad \left\{ \frac{\partial \ln \Omega_1(E_1)}{\partial E_1} + \frac{\partial \ln \Omega_2(E_2)}{\partial E_2} \frac{\partial E_2}{\partial E_1} \right\}_{E_1=\bar{E}_1} (E_1 - \bar{E}_1) + \\ &\quad \frac{1}{2} \left\{ \frac{\partial^2 \ln \Omega_1(E_1)}{\partial E_1^2} + \frac{\partial^2 \ln \Omega_2(E_2)}{\partial E_2^2} \left(\frac{\partial E_2}{\partial E_1} \right)^2 \right\}_{E_1=\bar{E}_1} (E_1 - \bar{E}_1)^2 + \dots \end{aligned}$$

The first term of this expansion is a constant, the second term vanishes as a result of equilibrium ($\beta_1 = \beta_2$), while the third term may be written as

$$\frac{1}{2} \left\{ \frac{\partial \beta_1}{\partial E_1} + \frac{\partial \beta_2}{\partial E_2} \right\}_{eq.} (E_1 - \bar{E}_1)^2 = -\frac{1}{2} \left\{ \frac{1}{kT_1^2(C_V)_1} + \frac{1}{kT_2^2(C_V)_2} \right\} (E_1 - \bar{E}_1)^2,$$

with $T_1 = T_2$. Ignoring the subsequent terms (which is justified if the systems involved are *large*) and taking the exponentials, we readily see that the function $\Omega^0(E_1)$ is a Gaussian in the variable $(E_1 - \bar{E}_1)$, with variance $kT^2(C_V)_1(C_V)_2 / \{(C_V)_1 + (C_V)_2\}$. Note that if $(C_V)_2 \gg (C_V)_1$ — corresponding to system 1 being in thermal contact with a very large reservoir — then the variance becomes simply $kT^2(C_V)_1$, regardless of the nature of the reservoir; cf. eqn. (3.6.3).

(b) If the systems involved are ideal classical gases, then $(C_V)_1 = \frac{3}{2}N_1k$ and $(C_V)_2 = \frac{3}{2}N_2k$; the variance then becomes $\frac{3}{2}k^2T^2 \cdot N_1N_2 / (N_1 + N_2)$. Again, if $N_2 \gg N_1$, we obtain the simplified expression $\frac{3}{2}N_1k^2T^2$; cf. Problem 3.18.

1.2. Since S is additive and Ω multiplicative, the function $f(\Omega)$ must satisfy the condition

$$f(\Omega_1\Omega_2) = f(\Omega_1) + f(\Omega_2). \quad (1)$$

Differentiating (1) with respect to Ω_1 (and with respect to Ω_2), we get

$$\Omega_2 f'(\Omega_1\Omega_2) = f'(\Omega_1) \quad \text{and} \quad \Omega_1 f'(\Omega_1\Omega_2) = f'(\Omega_2),$$

so that

$$\Omega_1 f'(\Omega_1) = \Omega_2 f'(\Omega_2). \quad (2)$$

Since the left-hand side of (2) is independent of Ω_2 and the right-hand side is independent of Ω_1 , each side must be equal to a constant, k , independent of both Ω_1 and Ω_2 . It follows that $f'(\Omega) = k / \Omega$ and hence

$$f(\Omega) = k \ln \Omega + \text{const.} \quad (3)$$

Substituting (3) into (1), we find that the constant of integration is zero.

1.4. Instead of eqn. (1.4.1), we now have

$$\Omega \propto V(V - v_0)(V - 2v_0)\dots(V - \overline{N-1}v_0),$$

so that

$$\ln \Omega = C + \ln V + \ln(V - v_0) + \ln(V - 2v_0) + \dots + \ln(V - \overline{N-1}v_0),$$

where C is independent of V . The expression on the right may be written as

$$C + N \ln V + \sum_{j=1}^{N-1} \ln \left(1 - \frac{jv_0}{V} \right) = C + N \ln V + \sum_{j=1}^{N-1} \left(-\frac{jv_0}{V} \right) = C + N \ln V - \frac{N^2 v_0}{2V}.$$

Equation (1.4.2) is then replaced by

$$\frac{P}{kT} = \frac{N}{V} + \frac{N^2 v_0}{2V^2} = \frac{N}{V} \left(1 + \frac{Nv_0}{2V} \right), \text{ i.e.}$$

$$PV \left(1 + \frac{Nv_0}{2V} \right)^{-1} = NkT.$$

Since $Nv_0 \ll V$, $(1 + Nv_0 / 2V)^{-1} \approx 1 - Nv_0 / 2V$. Our last result then takes the form: $P(V - b) = NkT$,

where $b = \frac{1}{2} Nv_0$.

A little reflection shows that $v_0 = (4\pi / 3)\sigma^3$, with the result that

$$b = \frac{1}{2} N \cdot \frac{4\pi}{3} \sigma^3 = 4N \cdot \frac{4\pi}{3} \left(\frac{1}{2} \sigma \right)^3.$$

1.11. Clearly, the initial temperatures and the initial particle densities of the two gases (and hence of the mixture) are the same. The entropy of mixing may, therefore, be obtained from eqn. (1.5.4), with $N_1 = 4N_A$ and $N_2 = N_A$. We get

$$\begin{aligned} (\Delta S)^* &= k[4N_A \ln(5/4) + N_A \ln 5] \\ &= R[4 \ln(5/4) + \ln 5] = 2.502 R, \end{aligned}$$

which is equivalent to about 0.5 R per mole of the mixture.