

1. A hypothetical velocity distribution of an ideal gas has the form $G(v) = Ae^{-kv}$. (i) Does $G(v)$ satisfy the molecular chaos postulate? (ii) Find A from the normalization condition. (iii) Find the most probable speed, average speed, and the rms speed. (iv) Find the distribution function $g(v_x)$. Check if G factorizes as $G(v) = g(v_x)g(v_y)g(v_z)$.

Solution: (i) It is straightforward to see that $G(v)$ satisfies the molecular chaos postulate because it does not depend on the directions of the velocities. (ii) The normalization condition for the distribution function is $1 = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dv_x dv_y dv_z G(v) = 4\pi \int_0^{\infty} v^2 dv G(v) = \int_0^{\infty} dv f(v)$. Substituting the explicit form of $G(v)$, you obtain $1 = 4\pi A \int_0^{\infty} v^2 dv e^{-kv} = 4\pi A J_2(k)$, where $J_2(k) = \int_0^{\infty} dv v^2 e^{-kv}$. Using $J_0(k) = \int_0^{\infty} dv e^{-kv} = k^{-1}$ it follows that $J_2(k) = \frac{d^2}{dk^2} J_0(k) = \frac{2}{k^3}$. Therefore, $A = \frac{1}{4\pi} J_2(k) = \frac{k^3}{8\pi}$. (iii) The most probable speed v_m is defined by the maximum of $f(v)$, that is, $\max[v^2 e^{-kv}]$. Taking the derivative over v you obtain $0 = 2ve^{-kv} - kv^2 e^{-kv}$ and so $v_m = \frac{2}{k}$. The average speed is given by $\bar{v} = \int_0^{\infty} dv v f(v) = 4\pi A \int_0^{\infty} dv v^3 e^{-kv} = \frac{k^3}{2} J_3(k)$. Using $J_3(k) = -\frac{d}{dk} J_2(k) = \frac{6}{k^4}$, you finally obtain $\bar{v} = \frac{3}{k}$. The average square speed is given by $\overline{v^2} = \int_0^{\infty} dv v^2 f(v) = 4\pi A \int_0^{\infty} dv v^4 e^{-kv} = \frac{k^3}{2} J_4(k)$. Using $J_4(k) = -\frac{d}{dk} J_3(k) = \frac{24}{k^5}$, it follows that $\overline{v^2} = \frac{12}{k^2}$ and so $v_{\text{rms}} = \sqrt{\overline{v^2}} = \frac{2\sqrt{3}}{k}$. (iv) The distribution function for a single velocity component can be obtained by integrating $G(v)$ over the remaining velocity components $g(v_x) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dv_y dv_z G(\sqrt{v_x^2 + v_y^2 + v_z^2}) = 2\pi A \int_0^{\infty} v_{\perp} dv_{\perp} e^{-k\sqrt{v_x^2 + v_{\perp}^2}}$, where $v_{\perp} = \sqrt{v_y^2 + v_z^2}$. Changing to the new variable $u = v_{\perp}^2$, you obtain $g(v_x) = \pi A \int_0^{\infty} du e^{-k\sqrt{v_x^2 + u}} = \frac{2\pi A}{k^2} e^{-k|v_x|} (1 + k|v_x|)$ or finally $g(v_x) = \frac{k}{4} e^{-k|v_x|} (1 + k|v_x|)$. Obviously $G(v) \neq g(v_x)g(v_y)g(v_z)$, that is the distribution is not factorizable, and hence it is not a good distribution function. Still, you could investigate the properties of $g(v_x)$. Start with checking the normalization $\int_{-\infty}^{+\infty} dv_x g(v_x) = 2 \int_0^{\infty} dv_x g(v_x) = \frac{k}{2} \int_0^{\infty} dv_x e^{-kv_x} (1 + kv_x) = \frac{k}{2} [J_0(k) + kJ_1(k)] = \frac{k}{2} \left(\frac{1}{k} + k \frac{1}{k^2} \right) = 1$, as it should be. The average square velocity is $\overline{v_x^2} = \int_{-\infty}^{+\infty} dv_x v_x^2 g(v_x) = \frac{k}{2} [j_2(k) + kJ_3(k)] = \frac{k}{2} \left(\frac{2}{k^3} + k \frac{6}{k^4} \right) = \frac{4}{k^2}$. This is in accord with the result in (ii) as $\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = \overline{v^2}$.

2. Suppose you flip 1000 unbiased coins. (i) What is the probability of getting 500 heads and 500 tails? (Use Stirling's approximation.) (ii) What is the probability of getting 450 heads and 550 tails? (Use Stirling again.) (iii) Compute the above two probabilities using the Gaussian approximation. How do they compare? (iv) Compute $\ln \Omega$ and $\ln \omega_{\text{max}}$. How do they compare?

Solution: (i) Obtain an expression for the thermodynamic probability using Stirling's approximation: $\omega(N_1) = \frac{N!}{N_1!(N-N_1)!} \simeq \frac{\sqrt{2\pi N} \left(\frac{N}{e}\right)^N}{\sqrt{2\pi N_1} \left(\frac{N_1}{e}\right)^{N_1} \sqrt{2\pi(N-N_1)} \left(\frac{N-N_1}{e}\right)^{N-N_1}} = \sqrt{\frac{N}{2\pi N_1(N-N_1)}} \frac{N^N}{N_1^{N_1} (N-N_1)^{N-N_1}}$. Evaluate this expression at $N_1 = 500$ to obtain $\omega(500) = \omega_{\text{max}} = \frac{1000!}{500!500!} \simeq \sqrt{\frac{1}{500\pi}} 2^{1000}$. Since, $\Omega = 2^{1000}$, it follows that $p(500) \simeq 2.5\%$. (ii) $\omega(450) = \frac{1000!}{450!550!} \simeq \sqrt{\frac{1000}{2\pi 450 \times 550}} \frac{1000^{1000}}{450^{450} 550^{550}}$ and so $p(450) \simeq 0.017\%$. (iii) The Gaussian approximation for the binomial distribution is $P(N_1) =$

$\sqrt{\frac{2}{\pi N}} e^{-2N(\frac{N_1}{N} - \frac{1}{2})^2}$, so $P(500) = \sqrt{\frac{2}{1000\pi}} e^{-2000(\frac{1}{2} - \frac{1}{2})^2} = \sqrt{\frac{2}{1000\pi}}$ and $P(450) = \sqrt{\frac{2}{1000\pi}} e^{-2000(\frac{450}{1000} - \frac{1}{2})^2}$. The ratio is $\frac{P(450)}{P(500)} = e^{-5}$. (iv) For the Stirling's approximation $\ln \Omega - \ln \omega_{\max} = 1000 \ln 2 + \frac{1}{2} \ln(500\pi) - 1000 \ln 2 = \frac{1}{2} \ln(500\pi)$; for the Gaussian approximation $\ln \Omega - \ln \omega_{\max} = -\ln \frac{\omega_{\max}}{\Omega} = -\ln P(500) = \frac{1}{2} \ln(500\pi)$.

3. A drunk person is walking along the x axis. He starts at $x = 0$, and his step size is $L = 0.5$ meters. For each step, he has chance $2/3$ of walking forwards (positive x) and chance $1/3$ of walking backwards (negative x). What is his expected position, \bar{x} , after 50 steps? What is the expected RMS variation around \bar{x} , $\Delta x_{\text{rms}} = \sqrt{(x - \bar{x})^2}$ after 50 steps?

Solution: $x = L(N_1 - N_2) = L(2N_1 - N)$, $\bar{x} = L \times 50 \times (\frac{2}{3} - \frac{1}{3})$, $\Delta x_{\text{rms}} = \sqrt{x^2 - \bar{x}^2} = 2L\sqrt{Npq}$.

4. Suppose that a system has allowed energy levels $n\varepsilon$, with $n = 0, 1, 2, 3, 4, \dots$. There are three distinguishable particles, with total energy $U = 4\varepsilon$. (i) Tabulate all possible distributions of the three particles among the energy levels, satisfying $U = 4\varepsilon$. (ii) Evaluate ω_k for each of above distributions, and also $\Omega = \sum_k \omega_k$. (iii) Calculate the average occupation numbers $\bar{N}_n = \sum_k N_n^{(k)} \omega_k / \Omega$ for the three particles in the energy states. Here \bar{N}_n is the average occupation number of the energy level with energy $n\varepsilon$. You should find \bar{N}_n for all $n \leq 4$ (and find that $\bar{N}_n > 4 = 0$).

Solution: (i)

$$\begin{aligned} U = 4\varepsilon &= 0\varepsilon \times 2 + 1\varepsilon \times 0 + 2\varepsilon \times 0 + 3\varepsilon \times 0 + 4\varepsilon \times 1 \\ &= 0\varepsilon \times 1 + 1\varepsilon \times 1 + 2\varepsilon \times 0 + 3\varepsilon \times 1 + 4\varepsilon \times 0 \\ &= 0\varepsilon \times 0 + 1\varepsilon \times 2 + 2\varepsilon \times 1 + 3\varepsilon \times 0 + 4\varepsilon \times 0 \\ &= 0\varepsilon \times 0 + 1\varepsilon \times 0 + 2\varepsilon \times 2 + 3\varepsilon \times 0 + 4\varepsilon \times 0 \end{aligned}$$

(ii) $\omega_{2,0,0,0,1} \frac{3!}{2!1!} = 3$, $\omega_{1,1,0,1,0} = \frac{3!}{1!1!1!} = 6$, $\omega_{0,2,1,0,0} = \frac{3!}{2!1!} = 3$, $\omega = \frac{3!}{2!1!} = 3$, $\Omega = \sum_k \omega_k = 15$. (iii)

$$\begin{aligned} N_0 &= \frac{1}{\Omega} (2 \times \omega_{2,0,0,0,1} + 1 \times \omega_{1,1,0,1,0} + 0 \times \omega_{0,2,1,0,0} + 1 \times \omega_{1,0,2,0,0}) \\ N_1 &= \frac{1}{\Omega} (0 \times \omega_{2,0,0,0,1} + 1 \times \omega_{1,1,0,1,0} + 2 \times \omega_{0,2,1,0,0} + 0 \times \omega_{1,0,2,0,0}) \\ N_2 &= \frac{1}{\Omega} (0 \times \omega_{2,0,0,0,1} + 0 \times \omega_{1,1,0,1,0} + 1 \times \omega_{0,2,1,0,0} + 2 \times \omega_{1,0,2,0,0}) \\ N_3 &= \frac{1}{\Omega} (0 \times \omega_{2,0,0,0,1} + 1 \times \omega_{1,1,0,1,0} + 0 \times \omega_{0,2,1,0,0} + 0 \times \omega_{1,0,2,0,0}) \\ N_4 &= \frac{1}{\Omega} (1 \times \omega_{2,0,0,0,1} + 0 \times \omega_{1,1,0,1,0} + 0 \times \omega_{0,2,1,0,0} + 0 \times \omega_{1,0,2,0,0}) \\ N_{n>4} &= 0 \end{aligned}$$

5. (i) Estimate the number of moles and molecules of water in all the Earth's oceans. Assume water covers 75% of the Earth to an average depth of 3 km. (ii) Estimate how many molecules of air are in each 2.0 liters breath you inhale that were also in the last breath Julius Caesar took. [Hint: Assume the atmosphere is about 10 km high and of constant density.] (iii) A space vehicle returning from the Moon enters the Earth's atmosphere at a speed of about 40,000 km/h. Molecules

(assume nitrogen) striking the nose of the vehicle with this speed correspond to what temperature? (Because of this high temperature, the nose of a space vehicle must be made of special materials, indeed part of it vaporize, and this is seen as a bright blaze upon reentry.)

Solution: (i) Since the average depth of the ocean is very small compared to the radius of the Earth, the ocean's volume can be calculated as that of a spherical shell with surface area $4\pi R_{\oplus}^2$ and a thickness Δy . Then use the density of sea water to find the mass and the molecular weight of water to find the number of moles. Volume = $0.754\pi R_{\oplus}^2 \Delta y = 0.754\pi(6.38 \times 10^6 \text{ m})^2 3 \times 10^3 \text{ m} = 1.15 \times 10^{18} \text{ m}^3$. Hence the number of moles = $1.15 \times 10^{18} \text{ m}^3 \left(\frac{1025 \text{ kg}}{\text{m}^3} \right) \left(\frac{1 \text{ mol}}{18 \times 10^{-3} \text{ kg}} \right) = 6.55 \times 10^{22}$, and the number of molecules = $6.55 \times 10^{22} \text{ moles} \left(\frac{6.02 \times 10^{23} \text{ molecules}}{1 \text{ mol}} \right) \approx 4 \times 10^{46}$. We assume that the last breath that Julius Caesar took has been spread uniformly throughout the atmosphere since his death. Calculate the number of molecules in JC last breath, and divide it by the volume of the atmosphere to get JC molecules per m^3 . Multiply that factor times the size of a breath to find the number of JC molecules in one of our breaths. $PV = NkT \Rightarrow N = \frac{PV}{kT} = \frac{1.01 \times 10^5 \text{ Pa} 2.0 \times 10^{-3} \text{ m}^3}{1.38 \times 10^{-23} \text{ J/K} 300 \text{ K}} = 4.9 \times 10^{22}$ molecules; atmospheric volume = $4\pi R_{\oplus}^2 h = 4\pi(6.38 \times 10^6 \text{ m})^2 1.0 \times 10^4 \text{ m} = 5.1 \times 10^{18} \text{ m}^3$, $\frac{\text{JC molecules}}{\text{m}^3} = \frac{4.9 \times 10^{22} \text{ molecules}}{5.8 \times 10^{18} \text{ m}^3} = 9.6 \times 10^3 \text{ molecules/m}^3$, and so $\frac{\# \text{JC molecules}}{\text{breath}} = 9.6 \times 10^3 \text{ molecules/m}^3 \times 2.0 \times 10^{-3} \text{ m}^3/\text{breath} = 19 \text{ molecules/breath}$. (iii) The temperature can be found from $v_{\text{rms}} = \sqrt{3kT/m}$, yielding $T = \frac{(28)(1.66 \times 10^{-27} \text{ kg})[4 \times 10^4 \text{ km/h}(1 \text{ ms}^{-1})/(3.6 \text{ kmh}^{-1})]^2}{3(1.38 \times 10^{-23} \text{ J/K})} = 1.4 \times 10^5 \text{ K}$.