

Week 3

Kinetic Theory of Gases / The First Law of Thermodynamics

3.1 Maxwell-Boltzmann Distribution

- 1/24:
- Applying the molecular partition function to the heat capacity of a water molecule.
 - A water molecule has three vibrational modes, which we will denote by ν_1, ν_2, ν_3 (corresponding to symmetric stretch, antisymmetric stretch, and bend).
 - Main takeaway: Heat capacity can change with temperature.
 - After a while (at several thousand kelvin), it will level off (see Figure 18.7).
 - Considers CO₂'s vibrational modes, too.
 - The infrared absorption of the bending mode is what's associated with the Greenhouse Effect.
 - The symmetric stretch is IR inactive due to its lack of change of dipole moment.
 - Raman active: Change in the polarizability of the molecule.
 - The Maxwell-Boltzmann distribution.
 - Maxwell derived it long before Boltzmann, but Boltzmann's thermodynamic derivation is much easier.
 - We know from the Boltzmann factor that $p(E) \propto e^{-E/k_B T}$.
 - Thus, to get the probability $p(v)$ of some speed v , we should have $p(v) \propto e^{-mv^2/2k_B T}$ times a constant giving the number of molecules of each speed? This yields

$$p(v) = A4\pi v^2 e^{-mv^2/2k_B T}$$

where A is a normalization constant.

- The Maxwell-Boltzmann distribution is such that

$$\begin{aligned} 1 &= \int_0^\infty p(v) \, dv \\ &= A \int_0^\infty 4\pi v^2 e^{-mv^2/2k_B T} \, dv \\ &= A \int_0^\infty 4\pi \left(\frac{2k_B T}{m} \right)^{3/2} u^2 e^{-u^2} \, du \\ &= A4\pi \left(\frac{2k_B T}{m} \right)^{3/2} \int_0^\infty u^2 e^{-u^2} \, du \end{aligned}$$

$$= A4\pi \left(\frac{2k_B T}{m} \right)^{3/2} \frac{\sqrt{\pi}}{4}$$

$$A = \left(\frac{m}{2\pi k_B T} \right)^{3/2}$$

– Therefore,

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

– Any distribution that doesn't look like this isn't in thermal equilibrium.

- A system with all particles having $v = 0$ is at thermal equilibrium with $T = 0$ K.
- A system with all particles having constant velocity in the same direction is at thermal equilibrium with $T = 0$ K.
 - Think relativity; if you're moving with them, it looks like they're not moving and thus this case is the same as the last one because your movement doesn't affect the thermodynamics of that system.
- A system with all particles having constant velocity in different directions is not at thermal equilibrium since it does not fit the bell curve but is rather a spike.

3.2 The First Law of Thermodynamics

1/26:

- See Labalme (2021b) for background on/content of today's lecture.
- Joule best quantified how we think about work and energy.
- **System:** Part of the world being investigated. It can contain energy, a number of particles, etc.
- The Newtonian way to change the energy into a system is to do work (mechanical, electrical, etc.) on the system. In chemistry, δw is positive if work is done on the system.
 - We have that

$$\delta w = -P dV$$

- A system at thermal equilibrium has a given temperature characteristic of the system. Some property of the system indicates how hot or cold it is (e.g., volume of mercury, etc.)
- Measure heat transfer using a calorimeter and a thermometer.
 - Convention: Heat put into a system δq is positive and this heat is transferred if the temperature is lower than another system or surroundings.
 - The heat capacity of a system times the change in temperature is equal to the heat put into the system. It is always positive as heat put into the system raises the temperature.
- Example molar heat capacities.
 - For water vapor at low pressure and 20 °C, $\overline{C}_V = 3R = 25 \text{ J mol}^{-1} \text{ K}^{-1}$.
 - For liquid water, it's higher (hydrogen bonding).
 - For ice, it's lower.
- **First law of thermodynamics:** The internal energy of a system changes with heat put into the system and work done on the system.

$$dU = \delta q + \delta w$$

– Note that in engineering, $dU = \delta q - \delta w$.

- **State variable:** A property that describes the system.
 - For example, a system of gas molecules has a state defined by the state variables T , P , V , and n .
- **State function:** A property that depends only upon the state of the system.
 - For example, some equations of state for an ideal gas are $PV = nRT$ or $PV = 2U/3$.
 - The internal energy is a state function.
 - Heat and work are not state functions because they do not depend uniquely on the values at equilibrium.
 - They also depend on the way you do something.
- **Reversible process:** A process that can be represented as a path along state variables, e.g., a line on a PV diagram. This implies that it is also a path where all state variables are known, and is therefore a path where the system is always in quasi-equilibrium.
 - Isothermal, isochoric, isobaric, and adiabatic changes are reversible.
 - All of these processes are analyzed exactly as in Labalme (2021b).
- **Irreversible process:** A process that cannot be drawn on a PV diagram.
- Experiment to measure γ (the ratio of specific heats):
 1. Let sit at $P_0 T_0$.
 2. Pump in a little gas (add Δn) and let sit, measure $P_0 + \Delta P_1, T_0$.
 3. Open the valve to air quickly to P_0 . Adiabatic expansion (cools down).
 4. Let sit to measure the new pressure $P + \Delta P_2$ when T is back at T_0 .
 5. γ is determined from $\Delta P_1, \Delta P_2$ (this will be a homework problem).
 - In the second step, we add some molecules into the container. We can show that $\Delta P_1/P_0 = \Delta N_1/n_0$.
 - In the third step, we let out the air, and we can show that $\Delta n_2/n_0 = \gamma \Delta P_1/P_0$.
 - In step 4, we have in the container $(n_0 + \Delta n_1 - \Delta n_2)RT_0 = (P_0 + \Delta P_2)V_0$.
 - This implies that $\Delta P_2/\Delta P_1 = 1 - 1/\gamma$.

3.3 Enthalpy

- 1/28:
- Thermodynamic derivation of the formula for $\langle P \rangle$ in terms of Q .
 - We have that

$$\begin{aligned}
 U &= \sum p_j E_j \\
 dU &= \sum (dp_j E_j + p_j dE_j) \\
 &= \underbrace{\sum dp_j E_j}_{\delta q} + \underbrace{\sum p_j \frac{\partial E_j}{\partial V} dV}_{-P}
 \end{aligned}$$

where the last part follows by analogy with $dU = \delta q - P dV$.

- It follows that

$$P = - \sum p_j \frac{\partial E_j}{\partial V} = - \left\langle \frac{\partial E}{\partial V} \right\rangle$$

- Thus, we have that

$$\begin{aligned}
 P &= - \sum \frac{e^{-E_j/k_B T}}{Q} \frac{\partial E_j}{\partial V} \\
 &= \frac{1}{Q} \sum k_B T \cdot - \frac{1}{k_B T} e^{-E_j/k_B T} \frac{\partial E_j}{\partial V} \\
 &= k_B T \frac{1}{Q} \sum \frac{\partial}{\partial E_j} \left(e^{-E_j/k_B T} \right) \frac{\partial E_j}{\partial V} \\
 &= k_B T \frac{1}{Q} \sum \frac{\partial}{\partial V} \left(e^{-E_j/k_B T} \right) \\
 &= k_B T \frac{1}{Q} \frac{\partial Q}{\partial V} \\
 P &= k_B T \frac{\partial \ln Q}{\partial V}
 \end{aligned}$$

- Applies the formula to an ideal gas of independent, indistinguishable particles to derive the ideal gas law.
- **Enthalpy:** A state function representign the heat put into the system at constant pressure. *Denoted by H . Given by*

$$H = U + PV$$

- We have that

$$\begin{aligned}
 dH &= dU + P dV + V dP \\
 &= \delta q - P dV + P dV + V dP \\
 &= \delta q + V dP
 \end{aligned}$$

- At constant pressure ($dP = 0$), we have that $dH = \delta q$.
- At constant volume, we have that $dH = \delta q$ as well?

- **Constant-volume heat capacity.** The following expression. *Denoted by C_V . Given by*

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N}$$

- **Constant-pressure heat capacity.** The following expression. *Denoted by C_P . Given by*

$$C_P = \left(\frac{\partial H}{\partial T} \right)_{P,N}$$

- For an ideal gas,

$$\begin{aligned}
 dH &= dU + d(PV) \\
 &= nC_V dT + nR dT \\
 &= n(C_V + R) dT
 \end{aligned}$$

- Recall this result from Labalme (2021b).

- Considers heat diagrams.

- Recall the enthalpy of phase changes ΔH_{fus} , ΔH_{vap} , and ΔH_{sub} .
- It follows that

$$H(T) - H(T_0) = \int_{T_0}^T C_p dT + \sum \Delta H_{\text{phase changes}}$$

- **Hess's Law:** $\Delta H = 0$ around a closed loop.
 - This is because H is a state function.
- **Standard enthalpy of formation.** Denoted by ΔH_f° . Units **kJ/mol**.
 - Calculated from the constituent elements in their standard state, 1 bar, 298.15 K.
- We have, for example, that the $\Delta H_{\text{vap}}^\circ$ of a substance is the difference of its ΔH_f° in its gaseous state and its ΔH_f° in its liquid state.
- With the standard enthalpy of formation and the heat capacity $C_P(T)$, one gets the enthalpy of formation at nonstandard temperatures.
- To get the enthalpy of formation at non-standard pressures of chemical interest, most of the effect is from the gas components because solids and liquid enthalpy vary little with pressure.
- The direction of change is sometimes in the direction of *positive* enthalpy change.
 - This change is driven by the fact that in these cases, the direction of change is toward the most probable state.
- In a reversible process, $dU = \delta q_{\text{rev}} - P dV$. In this case

$$\delta q_{\text{rev}} = dU + P dV = nC_V dT + P dV \neq dnC_V T + PV$$

so δq_{rev} is not a state function.

- However,

$$\begin{aligned} \frac{\delta q_{\text{rev}}}{T} &= nC_V \frac{dT}{T} + \frac{P dV}{T} \\ &= nC_V \frac{dT}{T} + nR \frac{dV}{V} \\ &= d(nC_V \ln T + nR \ln V) \end{aligned}$$

is a state function.

3.4 Chapter 25: The Kinetic Theory of Gases

From McQuarrie and Simon (1997).

1/30:

- **Kinetic theory of gases:** A simple model of gases in which the molecules (pictured as hard spheres) are assumed to be in constant, incessant motion, colliding with each other and with the walls of the container.
- McQuarrie and Simon (1997) does the KMT derivation of the ideal gas law from Labalme (2021a). Some important notes follow.
 - McQuarrie and Simon (1997) emphasizes the importance of

$$PV = \frac{1}{3}Nm \langle u^2 \rangle$$

as a fundamental equation of KMT, as it relates a macroscopic property PV to a microscopic property $m \langle u^2 \rangle$.

- In Chapter 17-18, we derived quantum mechanically, and then from the partition function, that the average translational energy $\langle E_{\text{trans}} \rangle$ for a single particle of an ideal gas is $\frac{3}{2}k_B T$. From classical mechanics, we also have that $\langle E_{\text{trans}} \rangle = \frac{1}{2}m \langle u^2 \rangle$. *This* is why we may let

$$\frac{1}{2}m \langle u^2 \rangle = \frac{3}{2}k_B T$$

recovering that the average translational kinetic energy of the molecules in a gas is directly proportional to the Kelvin temperature.

- **Isotropic** (entity): An object or substance that has the same properties in any direction.
 - For example, a homogeneous gas is isotropic, and this is what allows us to state that $\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$.
- McQuarrie and Simon (1997) derives

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

- u_{rms} is an estimate of the average speed since $\langle u^2 \rangle \neq \langle u \rangle^2$ in general.
- McQuarrie and Simon (1997) states without proof that the speed of sound u_{sound} in a monatomic ideal gas is given by

$$u_{\text{sound}} = \sqrt{\frac{5RT}{3M}}$$

- Assumptions of the kinetic theory of gases.
 - Particles collide elastically with the wall.
 - Justified because although each collision will not be elastic (the particles in the wall are moving too), the average collision will be elastic.
 - Particles do not collide with each other.
 - Justified because “if the gas is in equilibrium, on the average, any collision that deflects the path of a molecule... will be balanced by a collision that replaces the molecule” (McQuarrie & Simon, 1997, p. 1015).
- Note that we can do the kinetic derivation at many levels of rigor, but more rigorous derivations offer results that differ only by constant factors on the order of unity.
- Deriving a theoretical equation for the distribution of the *components* of molecular velocities.
 - Let $h(u_x, u_y, u_z) du_x du_y du_z$ be the fraction of molecules with velocity components between u_j and $u_j + du_j$ for $j = x, y, z$.
 - Assume that the each component of the velocity of a molecule is independent of the values of the other two components¹. It follows statistically that

$$h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

- Note that we use just one function f for the probability distribution in each direction because the gas is isotropic.
- We can use the isotropic condition to an even greater degree. Indeed, it implies that any information conveyed by u_x is necessarily and sufficiently conveyed by u_y , u_z , and u . Thus, we may take

$$h(u) = h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

¹This can be proven.

- It follows that

$$\frac{\partial \ln h(u)}{\partial u_x} = \frac{\partial}{\partial u_x} (\ln f(u_x) + \text{terms not involving } u_x) = \frac{d \ln f(u_x)}{du_x}$$

- Since

$$\begin{aligned} u^2 &= u_x^2 + u_y^2 + u_z^2 \\ \frac{\partial}{\partial u_x}(u^2) &= \frac{\partial}{\partial u_x}(u_x^2 + u_y^2 + u_z^2) \\ 2u \frac{\partial u}{\partial u_x} &= 2u_x \\ \frac{\partial u}{\partial u_x} &= \frac{u_x}{u} \end{aligned}$$

we have that

$$\begin{aligned} \frac{\partial \ln h}{\partial u_x} &= \frac{d \ln h}{du} \frac{\partial u}{\partial u_x} = \frac{u_x}{u} \frac{d \ln h}{du} \\ \frac{d \ln h(u)}{u du} &= \frac{d \ln f(u_x)}{u_x du_x} \end{aligned}$$

which generalizes to

$$\frac{d \ln h(u)}{u du} = \frac{d \ln f(u_x)}{u_x du_x} = \frac{d \ln f(u_y)}{u_y du_y} = \frac{d \ln f(u_z)}{u_z du_z}$$

- Since u_x, u_y, u_z are independent, we know that the above equation is equal to a constant, which we may call $-\gamma$. It follows that for any $j = x, y, z$, we have that

$$\begin{aligned} \frac{d \ln f(u_j)}{u_j du_j} &= -\gamma \\ \frac{1}{f} \frac{df}{du_j} &= -\gamma u_j \\ \int \frac{df}{f} &= \int -\gamma u_j du_j \\ \ln f &= -\frac{\gamma}{2} u_j^2 + C \\ f(u_j) &= A e^{-\gamma u_j^2} \end{aligned}$$

where we have incorporated the $1/2$ into γ .

- To determine A and γ , we let arbitrarily let $j = x$. Since f is a continuous probability distribution, we may apply the normalization requirement.

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} f(u_x) du_x \\ &= 2A \int_0^{\infty} e^{-\gamma u_x^2} du_x \\ &= 2A \sqrt{\frac{\pi}{4\gamma}} \\ A &= \sqrt{\frac{\gamma}{\pi}} \end{aligned}$$

- Additionally, since we have that $\langle u_x^2 \rangle = \frac{1}{3} \langle u^2 \rangle$ and $\langle u^2 \rangle = 3RT/M$, we know that $\langle u_x^2 \rangle = RT/M$. This combined with the definition of $\langle u_x^2 \rangle$ as a continuous probability distribution yields

$$\begin{aligned} \frac{RT}{M} &= \langle u_x^2 \rangle \\ &= \int_{-\infty}^{\infty} u_x^2 f(u_x) du_x \\ &= 2\sqrt{\frac{\gamma}{\pi}} \int_0^{\infty} u_x^2 e^{-\gamma u_x^2} du_x \\ &= 2\sqrt{\frac{\gamma}{\pi}} \cdot \frac{1}{4\gamma} \sqrt{\frac{\pi}{\gamma}} \\ &= \frac{1}{2\gamma} \\ \gamma &= \frac{M}{2RT} \end{aligned}$$

- Therefore,

$$f(u_x) = \sqrt{\frac{M}{2\pi RT}} e^{-Mu_x^2/2RT}$$

- It is common to rewrite the above in terms of molecular quantities m and k_B .
- It follows that as temperature increases, more molecules are likely to be found with higher component velocity values.
- We can use the above result to show that

$$\langle u_x \rangle = \int_{-\infty}^{\infty} u_x f(u_x) du_x = 0$$

- We can also calculate that $\langle u_x^2 \rangle = RT/M$ and $m \langle u_x \rangle^2 / 2 = k_B T / 2$ from the above result.
 - An important consequence is that the total kinetic energy is divided equally into the x -, y -, and z -components.
- McQuarrie and Simon (1997) discusses how the Doppler effect applied to moving molecules emitting radiation makes spectral peaks wider than we'd normally predict in a phenomenon known as **Doppler broadening**.
- Deriving **Maxwell-Boltzmann distribution**.
 - Let the probability that a molecule has speed between u and $u + du$ be defined by a continuous probability distribution $F(u) du$. In particular, we have from the above isotropic condition that

$$\begin{aligned} F(u) du &= f(u_x) du_x f(u_y) du_y f(u_z) du_z \\ &= \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-m(u_x^2 + u_y^2 + u_z^2)/2k_B T} du_x du_y du_z \end{aligned}$$

- Considering F over a **velocity space**, we realize that we may express the probability distribution F as a function of u via $u^2 = u_x^2 + u_y^2 + u_z^2$ and the differential volume element in every direction over the sphere of equal velocities (a sphere by the isotropic condition) by $4\pi u^2 du = du_x du_y du_z$.
- Thus, the Maxwell-Boltzmann distribution in terms of speed is

$$F(u) du = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} u^2 e^{-mu^2/2k_B T} du$$

- **Maxwell-Boltzmann distribution:** The distribution of molecular speeds.

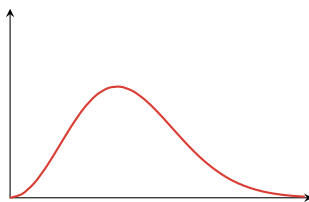


Figure 3.1: The Maxwell-Boltzmann distribution.

- **Velocity space:** A rectangular coordinate system in which the distances along the axes are u_x, u_y, u_z .
- We may use the above result to calculate that

$$\langle u \rangle = \sqrt{\frac{8RT}{\pi m}}$$

which only differs from u_{rms} by a factor of 0.92.

- **Most probable speed:** The most probable speed of a gas molecule in a sample that obeys the Maxwell-Boltzmann distribution. *Denoted by u_{mp} . Given by*

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

– Derived by setting $dF/du = 0$.

- We may also express the Maxwell-Boltzmann distribution in terms of energy via $u = \sqrt{2\varepsilon/m}$ and $du = d\varepsilon / \sqrt{2m\varepsilon}$ to give

$$F(\varepsilon) d\varepsilon = \frac{2\pi}{(\pi k_B T)^{3/2}} \sqrt{\varepsilon} e^{-\varepsilon/k_B T} d\varepsilon$$

- We can also confirm our previously calculated values for $\langle u^2 \rangle$ and $\langle \varepsilon \rangle$.
- McQuarrie and Simon (1997) does a higher-level derivation of the ideal gas law that is rather analogous to the one done in class (i.e., via its flux perspective).
- McQuarrie and Simon (1997) discusses a simple and Nobel-prize winning experiment that verified the Maxwell-Boltzmann distribution.