PHYS-3301

Lecture 22

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Presentations

3201-501 (11/19)

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Please send me the title of your presentation (20 min) by 11/14

Chapter. 9 Statistical Mechanics

Outline:

- Historical Overview
- The Boltzmann Distribution
- Maxwell Velocity Distribution
- Equipartition Theorem
- Maxwell Speed Distribution
- Classical and Quantum Statistics
- Fermi-Dirac Statistics
- Bose-Einstein Statistics

Maxwell Velocity Distribution

• $g(v_x) dv_x$ is the probability that the *x* component of a gas molecule's velocity lies between v_x and $v_x + dv_x$.



Maxwell Velocity Distribution

• The mean value of v_x^2				
$\overline{v_x^2} = C' \int_{-\infty}^{\infty} v_x^2 \exp\left(-\frac{1}{2}\beta m v_x^2\right) dv_x$				
$=2C'\int_0^\infty v_x^2 \exp\left(-\frac{1}{2}\beta m v_x^2\right) dv_x$				
$\overline{\nu_x^2} = \left(\frac{\beta m}{2\pi}\right)^{1/2} \frac{\sqrt{\pi}}{2} \left(\frac{2}{\beta m}\right)^{3/2} = \frac{1}{\beta m} = \frac{kT}{m}$				
$g^{(0)} = \frac{1}{1 + 1}$ The Maxwell velocity distribution as a function of one velocity dimension v _x				
$\overset{0.5g(0)}{\underset{0}{\overset{-}}}$ • The velocity component distributes around the peak at $v_x = 0$				
$\int_{\sqrt{\frac{1}{\beta m}}}^{1} = \sqrt{\frac{kT}{m}} \qquad \text{at} v_x = \sqrt{1/\beta m} = \sqrt{kT/m}, \ g(v_x) = g(0)e^{-1/2}$				

Maxwell Velocity Distribution

- Of course there is nothing special about x-direction, so the results for the x, y, and z velocity components are identical.
- The mean translational kinetic energy of a molecule:

$$\overline{K} = \overline{\frac{1}{2}mv^2} = \frac{1}{2}m(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}) = \frac{1}{2}m\left(\frac{3kT}{m}\right) = \frac{3}{2}kT$$

- We have just confirmed one of the principal results of the kinetic theory!!!
- Purely statistical considerations is good evidence of the validity of this statistical approach to thermodynamics.

Equipartition Theorem

e.g. in a monatomic ideal gas (He), each molecule has

$$K = \frac{1}{2}mv^{2} = \frac{1}{2}m(v_{x}^{2} + v_{y}^{2} + v_{z}^{2})$$

- There are 3 independent phase space coordinates (v_x, v_y, v_z); 3 degrees of freedom.
- Mean kinetic energy is $3(\frac{1}{2}kT) = \frac{3}{2}kT$ per molecule.
- In a gas of N helium molecules, the total internal energy is

$$U = N\overline{E} = \frac{3}{2}N\overline{k}$$

- The heat capacity at constant volume is $C_V = \frac{3}{2}Nk$
- For the heat capacity for 1 mole,

$$c_V = \frac{3}{2}N_A k = \frac{3}{2}R = 12.5 \text{ J/K}$$

The ideal gas constant R = 8.31 J/K.

The Rigid Rotator Model

• For diatomic gases, consider the rigid rotator model.



- The molecule rotates about either the *x* or *y* axis.
 The corresponding rotational energies are ¹/₂ *I*_x ²/_x and ¹/₂ *I*_y ²/_y
- There are five degrees of freedom (three translational and two rotational).

Equipartition Theorem

Now, why don't we include rotations about the z-axis?

- In the quantum theory of the rigid rotator the allowed energy levels are $E = \frac{L^2}{2I} = \frac{\hbar^2 \ell (\ell + 1)}{2I}$ I = rotational inertia, / = quantum number equal to 0 or a positive integer
- From previous chapter, the mass of an atom is confined to a nucleus that magnitude is smaller than the whole atom.

 \longrightarrow I_z is smaller than I_x and I_y .

- \longrightarrow Only rotations about *x* and *y* are allowed.
- In some circumstances it is better to think of atoms connected to each other by a massless spring.
- The vibrational kinetic energy is $\frac{1}{2}m(dr/dt)^2$
- There are seven degrees of freedom (three translational, two rotational, and two vibrational).

Molar Heat Capacity

 $C_V = \frac{3}{2}N_A k = \frac{3}{2}R = 12.5 \text{ J/K}$

- The heat capacities of diatomic gases are temperature dependent, indicating that the different degrees of freedom are "turned on" at different temperatures.
- Example of H₂



9.4: Maxwell Speed Distribution

Reminder: Maxwell velocity distribution:

$$f(\overline{v}) d^{\beta} \overline{v} = C \exp\left(\frac{1}{2}\beta m v^{2}\right) d^{\beta} \overline{v}$$

where we know that $C = (C')^3 = \left(\frac{\beta m}{2\pi}\right)^3$



9.4: Maxwell Speed Distribution

• Reminder: Maxwell velocity distribution:

$$f(\overline{\nu}) d^{\beta} \overline{\nu} = C \exp\left(\frac{1}{2}\beta m \nu^{2}\right) d^{\beta} \overline{\nu}$$

where we know that $C = (C')^3 = \left(\frac{\beta m}{2\pi}\right)^3$

- Even though f(v) is a function of the speed (v) and not the velocity (v), this is a still a vector distribution because the probability eq contains the differential velocity element.
- So, it is useful to turn this into a speed distribution F(v).
- F(v) dv = the probability of finding a particle with speed between v and v + dv



 $\sigma_{\nu} = (\overline{\nu^2} - \overline{\nu}^2)^{1/2} = \left(\frac{3kT}{m} - \frac{8kT}{\pi m}\right)^{1/2} = \left[3 - \left(\frac{8}{\pi}\right)^{1/2} \left(\frac{kT}{m}\right)^{1/2} \approx 0.48\nu^*\right]$

 σ_{ν} in proportion to \sqrt{T}

 The most probable speed v*, the mean speed V, and the rootmean-square speed v_{rms} are all different.

Relative speed

9.5: Classical and Quantum Statistics

- If molecules, atoms, or subatomic particles are in the liquid or solid state, the Pauli exclusion principle prevents two particles with identical quantum states from sharing the same space.
- There is no restriction on particle energies in classical physics.
- There are only certain energy values allowed in quantum systems.

Classical Distributions

 Rewrite Maxwell speed distribution in terms of energy (rather than velocity). F(v) dv = F(E) dE

 $E = \frac{1}{2}mv^2$ dE = mv dv

$$dv = \frac{dE}{mv} = \frac{dE}{\sqrt{2mE}} \qquad F(v)dv = 4\pi C \exp\left(-\frac{1}{2}\beta mv^2\right)v^2 dv$$

With this, the speed distribution can be turned into an E distribution F(v) dv = F(E) dEF(E)

 $F(E) = \frac{8\pi C}{\sqrt{2}m^{3/2}} \exp(-\beta E) E^{1/2}$ where

Maxwell-Boltzmann energ

Classical Distributions $F(E) = \frac{8\pi C}{\sqrt{2m^{3/2}}} \exp(-\beta E) E^{1/2}$

- Boltzmann showed that the statistical factor $exp(-\beta E)$ is a characteristic of any classical system.
- Thus, define the Maxwell-Boltzmann factor for classical system:

$$F_{\rm MB} = A \exp(-\beta E)$$

A = normalization constant

The energy distribution for classical system will have the form

$$n(E) = g(E)F_{\rm MB}$$

- \square n(E) dE: the number of particles with energies between E and E + dE
- \Box q(E) : know as density of states, is the number of states available per unit energy range
- \Box F_{MB} : tells the relative probability that an energy state is occupied at a given temperature

Quantum Distributions

- Characteristic of indistinguishability that makes quantum statistics different from classical statistics.
- Suppose that we have a system of just 2 particles, each of which has an equal probability (0.5) of being in either of two energy states.
- The possible configurations for distinguishable particles in either of two energy states:

re	State 1	State 2		
	AB			
	А	В		
	В	А		
		AB		

 These 4 configurations are equally likely; therefore the probability of each is one-fourth (0.25).

Quantum Distributions

 However, if the two particles are indistinguishable, our probability table changes:

State 1	State 2
XX	
Х	Х
	XX

- Only 3 equally likely configurations. The probability of each is one-third (~0.33).
- Because some particles do not obey the Pauli exclusion principle, two kinds of quantum distributions are needed.
- Fermions:
 - Particles with half-spins that obey the Pauli principle.
- Bosons:
 - Particles with zero or integer spins that do not obey the Pauli principle.

Quantum Distributions

Fermi-Dirac distribution (valid for fermion):

$$n(E) = g(E)F_{\rm FD}$$

where
$$F_{FD} = \frac{1}{B_{FD} \exp(\beta E) + 1}$$

Bose-Einstein distribution (valid for boson):

$$n(E) = g(E)F_{BE}$$
Where $F_{BE} = \frac{1}{B_{BE} \exp(\beta E) - 1}$ $F(E) = \frac{8\pi C}{\sqrt{2m^{3/2}}}\exp(-\beta E)E^{1/2}$

- In each case B_i (*i* = 1 or 2) is a normalization factor.
- Both distributions reduce to the classical Maxwell-Boltzmann distribution when $B_i \exp(\beta E)$ is much greater than 1.
 - \rightarrow the Maxwell-Boltzmann factor A exp($-\beta E$) is much less than 1.



that the classical Maxwell-Boltzmann distribution can be used to replace either quantum distribution.

- The normalization constants for the distributions depend on the physical system being considered.
- Because bosons do not obey the Pauli exclusion principle, more bosons can fill lower energy states.

Fermi-Dirac F_{FD}

3kT

4kT

2kT

Energy E

kT

0

- Three graphs coincide at high energies the classical limit.
- Maxwell-Boltzmann statistics may be used in the classical limit.

Classical and Quantum Distributions

Table 9.2 Classical and Quantum Distributions

Distributors	Properties of the Distribution	Examples	Distribution Function
Maxwell- Boltzmann	Particles are identical but distinguishable	Ideal gases	$F_{\rm MB} = A \exp(-\beta E)$
Bose-Einstein	Particles are identical and indistinguishable with integer spin	Liquid ⁴ He, photons	$F_{\rm BE} = \frac{1}{B_{\rm BE} \exp\left(\beta E\right) - 1}$
Fermi-Dirac	Particles are identical and indistinguishable with half-integer spin	Electron gas (free electrons in a conductor)	$F_{\rm FD} = \frac{1}{B_{\rm FD} \exp(\beta E) + 1}$