Phys 446: Solid State Physics / Optical Properties

Lattice vibrations: Thermal, acoustic, and optical properties

Fall 2007

Material to be included in the test Oct. 12th 2007

- Crystalline structures
  - 7 crystal systems and 14 Bravais lattices
- Crystallographic directions and Miller indices
  \[ d_{hk1} = \frac{n}{\sqrt{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)}} \]
- Definition of reciprocal lattice vectors:
  \[ b_1 = \frac{2\pi}{V} a_2 \times a_3, \quad b_2 = \frac{2\pi}{V} a_3 \times a_1, \quad b_3 = \frac{2\pi}{V} a_1 \times a_2 \]
- What is Brillouin zone
- Bragg formula:
  \[ 2d \sin \theta = m\lambda; \quad \Delta k = G \]

Last week:
- Phonons

Today:
- Einstein and Debye models for thermal capacity
- Thermal conductivity
- HW2 discussion

Factors affecting the diffraction amplitude:
- Atomic scattering factor (form factor):
  \[ f_a = \int n(r) e^{i\Delta k \cdot r} d^3 r \]
- In case of spherical distribution
  \[ f_a = \int_0^r 4\pi r^2 n(r) \frac{\sin(\Delta k \cdot r)}{\Delta k \cdot r} dr \]
- Structure factor
  \[ F = \sum_j f_{aj} e^{2\pi i(hu_j + kv_j + lw_j)} \]

Elastic stiffness and compliance. Strain and stress: definitions and relation between them in a linear regime (Hooke's law):
  \[ \sigma_{ij} = \sum_{kl} C_{ijkl} \varepsilon_{kl} \]
  \[ \varepsilon_{ij} = \sum_{kl} S_{ijkl} \sigma_{kl} \]

Elastic wave equation:
  \[ \frac{\partial^2 u}{\partial t^2} = \frac{C_{eff}}{\rho} \frac{\partial^2 u}{\partial x^2} \]
  sound velocity \[ v = \sqrt{\frac{C_{eff}}{\rho}} \]
Lattice vibrations: acoustic and optical branches
In three-dimensional lattice with \( s \) atoms per unit cell there are
\( 3s \) phonon branches: 3 acoustic, \( 3s - 3 \) optical

- Phonon - the quantum of lattice vibration.
  Energy \( \hbar \omega \); momentum \( \hbar \mathbf{q} \)

- Concept of the phonon density of states
- Einstein and Debye models for lattice heat capacity.
  Debye temperature
  \[ \theta_D = \frac{\hbar \nu}{k_B \left( \frac{6 \pi^2 N}{V} \right)^{1/3}} \]
  Low and high temperatures limits of Debye and Einstein models
- Formula for thermal conductivity
  \[ K = \frac{1}{3} Cv_l \]
- Be able to obtain scattering wave vector or frequency from geometry and data for incident beam (x-rays, neutrons or light)

### Summary of the Last Lecture
- Elastic properties – crystal is considered as continuous anisotropic medium
- Elastic stiffness and compliance tensors relate the strain and the stress in a linear region (small displacements, harmonic potential)
  Hooke's law:
  \[ \sigma_{ij} = \sum_{kl} C_{ijkl} \varepsilon_{kl} \]
  \[ \varepsilon_{ij} = \sum_{kl} S_{ijkl} \sigma_{kl} \]
- Elastic waves
  \[ \frac{\partial^2 u}{\partial t^2} - \frac{C_{eff}^2}{\rho} \frac{\partial^2 u}{\partial x^2} = 0 \]
  sound velocity
  \[ v = \sqrt{\frac{C_{eff}}{\rho}} \]
- Model of one-dimensional lattice: linear chain of atoms
- More than one atom in a unit cell – acoustic and optical branches
- All crystal vibrational waves can be described by wave vectors within the first Brillouin zone in reciprocal space

What do we need? 3D case consideration
Phonons. Density of states

### Three-dimensional lattice
In simplest 1D case with only nearest-neighbor interactions we had
equation of motion solution
\[ M \frac{\partial^2 u}{\partial t^2} = F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n) \]
\[ u(x,t) = Ae^{i(qx-vt)} \]

In general 3D case the equations of motion are:
\[ M_{\alpha} \frac{\partial^2 u_{\alpha}}{\partial t^2} = \sum_{m,\beta} F_{m\alpha}^{m\beta} \]
\( N \) unit cells, \( s \) atoms in each \( 3N's \) equations
Fortunately, have 3D periodicity \( \Rightarrow \)
Forces depend only on difference \( \mathbf{m-n} \)
Write displacements as
\[ u_{n\alpha}(x,t) = \frac{1}{\sqrt{M_\alpha}} u_{\alpha}(\mathbf{q}) e^{i(q\mathbf{r}_n - \omega t)} \]
Phonons
• Quantum mechanics: energy levels of the harmonic oscillator are quantized
• Similarly the energy levels of lattice vibrations are quantized.
• The quantum of vibration is called a **phonon** (in analogy with the photon - the quantum of the electromagnetic wave)

Allowed energy levels of the harmonic oscillator:
\[ E = (n + \frac{1}{2})\hbar\omega \]
where \( n \) is the quantum number

A normal vibration mode of frequency \( \omega \) is given by
\[ u = A e^{i(q\cdot r - \omega t)} \]

mode is occupied by \( n \) phonons of energy \( \hbar\omega \); momentum \( p = hq \)

Number of phonons is given by:
\[ n(\omega, T) = \frac{1}{e^{\hbar\omega/kT} - 1} \]

The total vibrational energy of the crystal is the sum of the energies of the individual phonons:
\[ E = \sum_{\psi} E_{\psi} = \sum_{\psi} (n_{\psi} + \frac{1}{2})\hbar\omega_{\psi}(q) \]

**Phonon Momentum**
• For all practical purposes, a phonon acts as if it carries a momentum \( p = hK \), which is sometimes called the crystal momentum.
• We have already seen examples of where this is used. For example, if an x-ray interacts with a lattice, then we know that the scattered ray(\( k' \)) and incident ray (\( k \)) have to be related by:
\[ k' = k + G \]
• Where \( G \) is a reciprocal lattice vector. In this process, the whole crystal recoils with momentum \(-hG\)

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**Phonon Momentum**

- If this photon interacts inelastically with the lattice, then we have:
  \[ \mathbf{k}' + \mathbf{K} = \mathbf{k} + \mathbf{G} \quad (\text{phonon is created}) \]
  \[ \mathbf{k}' = \mathbf{k} + \mathbf{K} + \mathbf{G} \quad (\text{phonon is absorbed}) \]

- Or:

**Density of states**

Consider 1D longitudinal waves. Atomic displacements are given by:

\[ u = A e^{i q x} \]

Boundary conditions: external constraints applied to the ends

**Periodic boundary condition:** \[ u(x = 0) = u(x = L) \]

Then \( e^{i q L} = 1 \) ⇒ condition on the admissible values of \( q \):

\[ q = \frac{2 \pi}{L} n \quad \text{where} \quad n = 0, \pm 1, \pm 2, \ldots \]

regularly spaced points, spacing \( 2\pi/L \).

Number of modes in the interval \( dq \) in \( q \)-space:

\[ \frac{L}{2\pi} \frac{dq}{dq} \]

Number of modes in the frequency range \((\omega, \omega + d\omega)\):

\[ D(\omega)d\omega = \frac{L}{2\pi} dq \]

\[ D(\omega) - \text{density of states} \]
determined by dispersion \( \omega = \omega(q) \)

**Density of states in 3D case**

Now have \( u = A e^{i(q_x+q_y+q_z)} \)

**Periodic boundary condition:**

\[ e^{i q_x L} = e^{i q_y L} = e^{i q_z L} = 1 \]

⇒ \( (q_x, q_y, q_z) = \left( \frac{2\pi}{L}, \frac{2\pi}{L}, \frac{2\pi}{L} \right) \)

\( l, m, n - \text{integers} \)

Plot these values in a \( q \)-space, obtain a 3D cubic mesh

number of modes in the spherical shell between the radii \( q \) and \( q + dq \):

\[ \left( \frac{L}{2\pi} \right)^3 4\pi q^2 dq = \frac{V}{(2\pi)^3} 4\pi q^2 dq \]

\[ V = L^3 - \text{volume of the sample} \]

⇒ **Density of states**

\[ D(\omega) = \frac{V q^2}{2\pi^3} \frac{1}{d\omega / dq} \]

**Few notes:**

- Equation we obtained is valid only for an isotropic solid.
  (vibrational frequency does not depend on the direction of \( q \))

- We have associated a single mode with each value of \( q \).
  This is not quite true for the 3D case: for each \( q \) there are 3 different
  modes, one longitudinal and two transverse.

- In the case of lattice with basis the number of modes is \( 3s \),
  where \( s \) is the number of non-equivalent atoms.
  They have different dispersion relations. This should be taken into
  account by index \( p = 1 \ldots 3s \) in the density of states.
Lattice specific heat (heat capacity)

Defined as (per mole) \( C = \frac{dQ}{dT} \) If constant volume \( V \)
\[ C_v = \left( \frac{\partial E}{\partial T} \right)_v \]

The total energy of the phonons at temperature \( T \) in a crystal:
\[ E = \sum_{q,p} \langle n_q \rangle \hbar \omega_p (q) = 0 \]  
(the zero-point energy is chosen as the origin of the energy).

\[ \langle n \rangle = \frac{1}{e^{\hbar \omega/kT} - 1} \]  - Planck distribution
Then \( E = \sum_{q,p} \frac{\hbar \omega_p (q)}{e^{\hbar \omega/kT} - 1} \)
replace the summation over \( q \) by an integral over frequency:
\[ E = \sum_p \int d\omega D_p(\omega) \frac{\hbar \omega}{e^{\hbar \omega/kT} - 1} \]
Then the lattice heat capacity is:
\[ C_v = \frac{\partial E}{\partial T} = k_B \sum_p \int d\omega D_p(\omega) \left( \frac{\hbar \omega}{k_B T} \right)^2 e^{\hbar \omega/kT} \]

Central problem is to find the density of states

Debye model

• assumes that the acoustic modes give the dominant contribution to the heat capacity
• Within the Debye approximation the velocity of sound is taken a constant independent of polarization (as in a classical elastic continuum)

The dispersion relation: \( \omega = \nu q \), \( \nu \) is the velocity of sound.

In this approximation the density of states is given by:
\[ D(\omega) = \frac{Vq^2}{2\pi^2} \frac{1}{d\omega/dq} = \frac{Vq^2}{2\pi^2} \frac{1}{v} = \frac{V\omega^2}{2\pi^2 v^3} \]

Need to know the limits of integration over \( \omega \). The lower limit is 0. How about the upper limit? Assume \( N \) unit cells is the crystal, only one atom in per cell \( \Rightarrow \) the total number of phonon modes is \( 3N \)
\[ \sum_p \int_0^{\omega_D} D(\omega)d\omega = 3N \]  \( \Rightarrow \) \( \omega_D = \left( \frac{6\pi^2 v^3 N}{V} \right)^{\frac{1}{3}} = v(6\pi^2 n)^{\frac{1}{3}} \)  - Debye frequency

The cutoff wave vector which corresponds to this frequency is
\[ q_D = \frac{\omega_D}{v} = \left( \frac{6\pi^2 N}{V} \right)^{\frac{1}{3}} \]  modes of wave vector larger than \( q_D \) are not allowed - number of modes with \( q \leq q_D \) exhausts the number of degrees of freedom

Then the thermal energy is
\[ E = 3 \int_0^{\omega_D} d\omega \frac{V \omega^3}{2\pi^2 v^3} \frac{\hbar \omega}{e^{\hbar \omega/k_BT} - 1} \]
where is "3" from ?
\[ \int_0^{\omega_D} \frac{d\omega}{e^{\hbar \omega/k_BT} - 1} = \frac{3V^k_B^4 T^4}{2\pi^2 v^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1} \]
where \( x_D = \hbar \omega_D/k_BT \) and \( x_D = \hbar \omega_D/k_BT = \theta_D/T \)

Debye temperature:
\[ \theta_D = \frac{\hbar V}{k_B} \left( \frac{6\pi^2 N}{V} \right)^{\frac{1}{3}} \]

The total phonon energy is then
\[ E = 9Nk_B T \left( \frac{T}{\theta_D} \right)^{\frac{3}{2}} \int_0^{x_D} dx \frac{x^3}{e^x - 1} \]
where \( N \) is the number of atoms in the crystal and \( x_D = \theta_D/T \)

To find heat capacity, differentiate
\[ E = \frac{3V^2}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar \omega/k_BT} - 1} \]
So,
\[ C_v = \frac{3V^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} d\omega \frac{\omega^4 e^{\hbar \omega/k_BT}}{(e^{\hbar \omega/k_BT} - 1)^2} = 9N k_B \left( \frac{T}{\theta_D} \right)^{\frac{3}{2}} \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2} \]

In the limit \( T >> \theta_D, x << 1 \) \( \Rightarrow \) \( C_v = 3Nk_B \) - Dulong-Petit law
Opposite limit, $T << \theta_D$: let the upper limit in the integral $x_D \rightarrow \infty$

Get

$$E = 9Nk_BT \left( \frac{T}{\theta_D} \right)^3 \int_0^\infty dx \frac{x^3}{e^x - 1} = 9Nk_BT \left( \frac{T}{\theta_D} \right)^3 \frac{\pi^4}{15} = \frac{3\pi^4}{5}Nk_BT \left( \frac{T}{\theta_D} \right)^3$$

⇒ $C_v = \frac{12\pi^4}{5}Nk_BT \left( \frac{T}{\theta_D} \right)^3$ \textit{within the Debye model at low temperatures} $C_v \propto T^3$

The Debye temperature is normally determined by fitting experimental data.

Curve $C_v(T/\theta)$ is universal – it is the same for different substances.

Real density of vibrational states is much more complicated than those described by the Debye and Einstein models.

This density of states must be taken into account in order to obtain quantitative description of experimental data.

The density of states for Cu.

The dashed line is the Debye approximation.

The Einstein approximation would give a delta peak at some frequency.

\textbf{Einstein model}

The density of states is approximated by a $\delta$-function at some $\omega_E$:

$$D(E) = N\delta(\omega - \omega_E)$$

where $N$ is the total number of atoms – simple model for optical phonons.

Then the thermal energy is

$$E = \frac{3N\hbar\omega_E}{e^{\frac{\hbar\omega_E}{k_BT}} - 1}$$

The heat capacity is then

$$C_v = \frac{\partial E}{\partial T} = 3Nk_B\left( \frac{\hbar\omega_E}{k_BT} \right)^2 e^{\frac{\hbar\omega_E}{k_BT}} \left( e^{\frac{\hbar\omega_E}{k_BT}} - 1 \right)^2$$

The high temperature limit is the same as that for the Debye model:

$C_v = 3Nk_B$ - the Dulong-Petit law.

At low temperatures $C_v \sim e^{-\hbar\omega_E/k_BT}$ - different from Debye $T^3$ law.

Reason: at low $T$ acoustic phonons are much more populated ⇒ the Debye model is much better approximation than the Einstein model.

\textbf{Summary}

- In three-dimensional lattice with $s$ atoms per unit cell there are $3s$ phonon branches: 3 acoustic, $3s - 3$ optical.
- \textbf{Phonon} - the quantum of lattice vibration.
  - Energy $\hbar\omega$; momentum $\hbar q$.
- \textbf{Density of states} is important characteristic of lattice vibrations;
  - It is related to the dispersion $\omega = \omega(q)$.
  - Simplest case of isotropic solid, for one branch: $D(\omega) = \frac{Vq^2}{2\pi^2} \frac{1}{d\omega/dq}$
- Heat capacity is related to the density of states.
- Debye model – good when acoustic phonon contribution dominates.
  - At low temperatures gives $C_v \propto T^3$.
- Einstein model - simple model for optical phonons ($\omega(q)$ is constant).
- At high $T$ both models lead to the Dulong-Petit law: $C_v = 3Nk_B$.
- Real density of vibrational states is more complicated.
**Thermal Conductivity**

Temperature gradient in a material → heat flow from the hotter to the cooler end.

*Heat current density* \( j \) (amount of heat flowing across unit area per unit time) is proportional to the temperature gradient \( \frac{dT}{dx} \):

\[
j_{u} = -K \frac{dT}{dx} \quad K \text{ - thermal conductivity}
\]

- In metals the heat is carried both by electrons and phonons; electron contribution is much larger
- In insulators, there are no mobile electrons ⇒ heat is transmitted entirely by phonons

**Heat transfer by phonons**

*phonon gas*: in every region of space there are phonons traveling randomly in all directions, much like the molecules in an ordinary gas

- phonon concentration is larger at the hotter end → they move to the cooler end
- the advantage of using this gas model: can apply familiar concepts of the kinetic theory of gases

**Dependence of the thermal conductivity on temperature**

- \( C \), dependence on temperature has already been discussed
- Sound velocity \( \nu \) essentially insensitive to temperature
- The mean free path \( l \) depends strongly on temperature

Three important mechanisms are to be considered:

(a) collision of a phonon with other phonons

(b) collision of a phonon with imperfections in the crystal

(c) collision of a phonon with the external boundaries of the crystal

The phonon-phonon scattering is due to the *anharmonic interaction*. If interatomic forces are purely harmonic – no phonon-phonon interaction.

At high temperature atomic displacements are large ⇒ stronger anharmonism ⇒ phonon-phonon collisions become more important

At high \( T \) the mean free path \( l \propto 1/T \): number of phonons \( n \propto T \) at high \( T \) collision frequency \( \propto n \Rightarrow l \propto 1/n \)

**Elementary kinetic considerations:**

if \( c \) is the heat capacity of the single particle, then moving from region with \( T+\Delta T \) to a \( T \), particle will give up energy \( c\Delta T \)

\( \Delta T \) between the ends of the free path length \( l_{x} \):

\[
\Delta T = \frac{dT}{dx} l_{x} = \frac{dT}{dx} \nu \tau
\]

where \( \tau \) is the average time between collisions

The net energy flux \( (n - \text{concentration}) \):

\[
j_{u} = -n\left(\nu v_{x}^{2}\right)\frac{dT}{dx} c \tau = -\frac{1}{3} n\left(\nu v_{x}^{2}\right) c \tau \frac{dT}{dx}
\]

for phonons, \( \nu \) is constant. \( nc = C; \ l = \nu \tau \)

\[
\Rightarrow j_{u} = -\frac{1}{3} Cv \frac{dT}{dx} \Rightarrow K = \frac{1}{3} Cv l \quad \text{- phonon thermal conductivity}
\]

Suppose that two phonons of vectors \( q_{1} \) and \( q_{2} \) collide, and produce a third phonon of vector \( q_{3} \).

Momentum conservation: \( q_{3} = q_{1} + q_{2} \)

\( q_{3} \) may lie inside the Brillouin zone, or not. If it’s inside → momentum of the system before and after collision is the same.

This is a *normal process*. It has no effect at all on thermal resistivity, since it has no effect on the flow of the phonon system as a whole.

If \( q_{3} \) lies outside the BZ, we reduce it to equivalent \( q_{4} \) inside the first BZ: \( q_{3} = q_{4} + G \)

Momentum conservation: \( q_{1} + q_{2} = q_{4} + G \)

The difference in momentum is transferred to the center of mass of the lattice.

This type of process is is known as the *umklapp process*

- highly efficient in changing the momentum of the phonon
- responsible for phonon scattering at high temperatures
The second mechanism - phonon scattering results from defects. Impurities and defects scatter phonons because they partially destroy the periodicity of the crystal.

At very low T, both phonon-phonon and phonon-defect collisions become ineffective:
- there are only a few phonons present,
- the phonons are long-wavelength ones not effectively scattered by defects, which are much smaller in size

In the low-temperature region, the primary scattering mechanism is the external boundary of the specimen - so-called size or geometrical effects.

Becomes effective because the phonon wavelengths are very long - comparable to the size of the sample $L$.

The mean free path here is $l \sim L$ ⇒ independent of temperature.

Anharmonism

So far, lattice vibrations were considered in harmonic approximation. Some consequences:
- Phonons do not interact; no decay
- No thermal expansion
- Elastic constants are independent of pressure and temperature
- Heat capacity is constant at high $T$ ($T >> \theta_D$).

Anharmonic terms in potential energy:

$$U(x) = cx^2 - gx^3 - fx^4$$

$x$ - displacement from equilibrium separation at $T = 0$

Techniques for probing lattice vibrations

- Inelastic X-ray scattering
- Neutron scattering
- Infrared spectroscopy
- Brillouin and Raman scattering

Inelastic X-ray scattering

Assumed $\Omega(q) << \omega_0$

true for x-rays:

$\hbar \Omega < 100 \text{ meV}; \ h\omega_0 \sim 10^4 \text{ eV}$

$n$ - index of refraction

Measuring $\omega - \omega_0$ and $\theta \sin \theta$ one can determine dispersion $\Omega(q)$

This difficulty can be overcome by use of neutron scattering

Energy of “thermal” neutrons is comparable with $\hbar \Omega$ (80 meV for $\lambda \approx 1 \text{ Å}$)
Brillouin and Raman spectroscopy

Inelastic light scattering mediated by the electronic polarizability of the medium

- a material or a molecule scatters irradiant light from a source
- Most of the scattered light is at the same wavelength as the laser source (elastic, or Raileigh scattering)
- but a small amount of light is scattered at different wavelengths (inelastic, or Raman scattering)

\[ \omega_i - \Omega(q) \]

\[ \omega_i + \Omega(q) \]

\[ \omega_i \]

\[ \alpha \]

\[ \beta \]

\[ \alpha \]

\[ \beta \]

\[ \lambda_i \]

\[ a_0 \]

\[ \lambda \rightarrow \lambda \gg a_0 \Rightarrow \text{only small wavevector (close to BZ center) phonons are seen in the 1st order (single phonon) Raman spectra of bulk crystals} \]

Analysis of scattered light energy, polarization, relative intensity provides information on lattice vibrations or other excitations

Summary

- Phonon thermal conductivity
  \[ K = \frac{1}{3} C v l \]

- Mechanisms of phonon scattering affecting thermal resistivity:
  - umklapp processes of phonon-phonons collision – important at high T
  - collision of a phonon with defects and impurities in the crystal
  - collision of a phonon with the external boundaries of the crystal – important at low T

- Anharmonism of potential energy is responsible for such effects as:
  - phonon-phonon interaction
  - thermal expansion

- Techniques for probing lattice vibrations:
  - Inelastic X-ray scattering, Neutron scattering, Infrared spectroscopy, Brillouin and Raman scattering
  - Electron energy loss spectroscopy

Raman scattering in crystalline solids

Not every crystal lattice vibration can be probed by Raman scattering. There are certain selection rules:

1. Energy conservation:
   \[ \hbar \omega_i = \hbar \omega_i \pm \hbar \Omega \]

2. Momentum conservation:
   \[ k_i = k_i + q \Rightarrow 0 \leq |q| \leq 2|k| \Rightarrow 0 \leq |q| \leq \frac{4m}{\lambda_i} \]

3. Selection rules determined by crystal symmetry

SOME USEFUL SLIDES FROM Physics-I
Avogadro’s number and Ideal Gases

In Eq. (20-1), Avogadro’s number is expressed in terms of mol⁻¹, which is the inverse mole, or 1 mol⁻¹. We could instead explicitly state the elementary unit involved in a given situation. For example, we might write \( N_A = 6.02 \times 10^{23} \) atoms/mole of H₂ if the elementary unit is an atom. If, instead, the elementary unit is a molecule, then we might write \( N_A = 6.02 \times 10^{23} \) molecules/mole.

Ideal Gases

\( pV = nRT \)  (ideal gas law)

\( k = \frac{R}{N_A} = \frac{8.31 \text{ J/mol} \cdot \text{K}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 1.38 \times 10^{-23} \text{ J/K} \)

Ideal Gas at Constant Temperature

\( p = nRT \frac{1}{V} = (\text{a constant}) \frac{1}{V} \)

\( R \) is a gas constant

The Kinetic Theory of Gases; Mole

One mole is the number of atoms in a 12 g sample of carbon-12

Avogadro’s Number

\( N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \)  (Avogadro’s number)

\[ n = \frac{N}{N_A} \]

\[ n = \frac{M_{\text{sam}}}{M} = \frac{m_{\text{sam}}}{mN_A} \]

\( M \) is molar mass;  \( m \) is molecular mass

Pressure, Temperature, and Speed of molecules

\( v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \)

\( mN_A \) is the molar mass \( M \)

Root-mean-square speed

The Distribution of Molecular Speeds

\[ P(v) = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} \nu^2 e^{-M\nu/2RT} \]

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mole Mass (g/mol)</th>
<th>( v_{\text{rms}} ) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H₂)</td>
<td>2.01</td>
<td>468</td>
</tr>
<tr>
<td>Nitrogen (N₂)</td>
<td>28</td>
<td>517</td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>32.0</td>
<td>493</td>
</tr>
<tr>
<td>Carbon dioxide (CO₂)</td>
<td>44.0</td>
<td>612</td>
</tr>
<tr>
<td>Water (H₂O)</td>
<td>18.0</td>
<td>645</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>16.0</td>
<td>457</td>
</tr>
</tbody>
</table>

For convenience, we often use the concept of 100% saturation to simplify our calculations.
**View at the molecular theory of an ideal Gas**

\[ C_v = \frac{3}{2} R \]

\[ C_p = C_v + R. \]

(a) He  
(b) O₂  
(c) CH₄

**Heat Transfer Mechanisms**

- Convection
- Radiation
- Conduction

**Specific Heats of Some Substances at Room Temperature**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific Heat</th>
<th>Molar Specific Heat</th>
<th>Bond R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental Solids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>0.8305</td>
<td>128</td>
<td>26.5</td>
</tr>
<tr>
<td>Tungsten</td>
<td>0.9231</td>
<td>134</td>
<td>24.8</td>
</tr>
<tr>
<td>Silver</td>
<td>0.8564</td>
<td>236</td>
<td>25.5</td>
</tr>
<tr>
<td>Copper</td>
<td>0.6923</td>
<td>336</td>
<td>24.5</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.215</td>
<td>900</td>
<td>24.4</td>
</tr>
<tr>
<td>Other Solids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brass</td>
<td>0.692</td>
<td>380</td>
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</tr>
<tr>
<td>Graphite</td>
<td>0.19</td>
<td>790</td>
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</tr>
<tr>
<td>Glass</td>
<td>0.20</td>
<td>840</td>
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</tr>
<tr>
<td>Ice (-10°C)</td>
<td>0.530</td>
<td>2220</td>
<td></td>
</tr>
<tr>
<td>LNG Gas</td>
<td>0.033</td>
<td>140</td>
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<tr>
<td>Ethyl alcohol</td>
<td>0.58</td>
<td>2430</td>
<td></td>
</tr>
<tr>
<td>Seawater</td>
<td>0.62</td>
<td>1200</td>
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</tr>
<tr>
<td>Water</td>
<td>1.80</td>
<td>4190</td>
<td></td>
</tr>
</tbody>
</table>

\[ Q = C_p \Delta T = C(G_f - T_i) \]

\[ Q = cm \Delta T = cm(T_f - T_i) \]

**Heat Capacity**

**Specific Heat**

\[ Q = kA(\Delta T/L)t, \]

Where \( k \) is the thermal conductivity.