Classical Physics at the Nanoscale
• At the nanoscale, classical physics begins to give way to quantum physics.

• **Classical physics often fails in describing behavior of electron systems, which are important in determining material properties such as electric, magnetic,...etc.**

• **However in some cases one can adequately describe many physical phenomena associated with nanoparticles.**

• **At small scale forces such as friction and surface tension dominate over forces such as gravity.**
Mechanical Frequency

- Cantilever beams are very important structures in many nano/micro-electro-mechanical systems (N/MEMS).
- The most important use of nanoscale cantilevers is in atomic force microscopy (AFM).
- The resonant frequency of a cantilever beam can be derived from Hooke’s law and the mass-spring model, \( F = -kx \), where \( F \) is force, \( m \) is mass and \( k \) is spring constant.
- Newton’s second law gives
  \[
  F = m \frac{d^2x}{dt^2} = kx
  \]
  where \( \omega = (k/m)^{1/2} \)
- The solution to the differential equation gives
  \[
  x = A \cos(\omega t + \phi)
  \]
  \( A \) is the amplitude and \( \phi \) is the phase of the oscillations.
The frequency $f$ relates to the oscillation period, $T$,

$$f = \frac{1}{T} = \frac{1}{2} = \frac{1}{2} \left(\frac{k}{m}\right)^{\frac{1}{2}}$$

$m$ varies with volume ($L^3$) and $k$ varies with $L$

$$\mu \frac{1}{L}$$

Hence the frequency is inversely proportional to length.
• Alternatively, if one thinks of a string oscillations, e. g. in a guitar or a violin – $\lambda = L/2$

• If the oscillator has only one node at one end (fixed at one end), e. g. a cantilever oscillator – $\lambda = L/4$

• Since $\lambda = vt$, where $t$ is the time for wave to travel one oscillation and $v$ is the wave velocity

\[
\frac{2}{t} = \left( \frac{v}{L} \right) \quad [\text{nodes at both ends}]
\]

\[
\frac{2}{t} = \left( \frac{v}{2L} \right) \quad [\text{nodes at one ends}]
\]

• Also, in wave mechanics

\[
v = \sqrt{\frac{T}{\rho}}
\]

$T$ is the string tension and $\rho$ is the mass per unit length.

• In three dimensional solid material $v$ can be written in terms of Young’s modulus, $E$.

\[
v = \sqrt{\frac{E}{\rho}}
\]

• The speed of sound in Si is $v = 8900 \text{ m/s}$, $\omega = 14 \text{ kHz}$ for a 1 m long cantilever and $\omega = 1.4 \text{ MHz}$ for 1 cm long cantilever.

• In a typical Si AFM cantilever with $k$ between $0.01 - 100 \text{ N/m}$ the resonant frequency is between $10 - 200 \text{ kHz}$. 
Viscosity

• Why do particles fall much more slowly?

• Stokes law gives the viscous force on a sphere of radius $R$, mass $m$, and density $r$ in a viscous medium of viscosity $\eta$ is

$$F = 6 \pi R \eta v$$

• The sphere reaches a terminal velocity $v_m$ when gravitational force is equal to viscous force, i.e.,

$$v_t = \frac{mg}{6 \pi R} = \frac{4}{3} \frac{R^3}{6} \frac{g}{R} = \frac{2}{9} \frac{gR^2}{\mu R^2}$$

• $v_t$ is proportional to $R$ and this is why particles fall much more slowly.

• Note that the above treatment is only valid under conditions of streamline flow, for small particles and small velocities. This condition is met when the Reynold’s Number, $Re$ defines below, is less than 2000

$$Re = \frac{2R v}{\mu} = \frac{\text{Inertia Force}(v)}{\text{Viscous Force}(\frac{v}{2R})}$$

• As size decreases, the ratio of inertia forces to viscous forces within the fluid decreases and viscosity dominates.
• Example:

– Consider an iron sphere of radius 1 mm and density 7000 kg/m$^3$ falling through water with $\eta = 0.01$ Pa s.
– Using the equations above $v_t$ for the sphere is 1 m/s.
– If the sphere is changes to 1 µm in radius $v_t$ becomes 1 µm/s; i.e., it falls by a distance equivalent to its size.
– If the radius is further reduced to 1 nm, $v_t$ drops to 1 pm/s, which is negligible compared to its size.
– Moreover we expect interactions of the nanoscale sphere with molecules of atoms and molecules in the fluid to impact the iron sphere more as we will discuss next (Brownian motion).
Brownian Motion at the Nanoscale

- Brownian motion was first observed by the British biologist Robert Brown and it is the random motion of particles in a fluid resulting from collisions with atoms and molecules.

- The 1D diffusive Brownian motion probability distribution as a function of $x$ and $t$, $P(x,t)$, is a Gaussian distribution

$P(x,t) = (4 \pi D t)^{3/2} \exp\left(-\frac{x^2}{4Dt}\right)$

- $D$ is the diffusivity of a particle of radius $R$ in a fluid of viscosity $\eta$ at temperature $T$ given by

$D = \frac{kT}{6\pi \eta R}$
• Using \( P(x,t) \) one can determine a characteristic 2D diffusion length, \( x_{rms} \)

\[
x_{rms} = (4Dt)^{\frac{1}{2}}
\]

• If we revisit the ion sphere (1 nm radius) example
  – The characteristic Brownian diffusion length per second is

\[
x_{rms} = 2D^2 \quad 9 \quad m
\]
  – 9 \( \mu \)m is much larger than 1 pm, and hence the Brownian diffusive motion is dominant for the 1 nm particle.

• If we revisit the ion sphere (1 \( \mu \)m radius) example
  – The characteristic Brownian diffusion length per second is

\[
x_{rms} = 2D^2 \quad 0.3 \quad m
\]
  – 0.3 \( \mu \)m is comparable to 1 \( \mu \)m/s. Hence both diffusive Brownian motion and viscous motion in the fluid are comparable and should both be taken into account.

• When both diffusive Brownian motion and viscous motion are both effective and in the presence of an external force, \( F_{ext} \), the Newton’s equation of motion takes the form

\[
F_{ext} + F_R(t) \quad (6 \quad R) \quad \frac{dx}{dt} = \left( \frac{4}{3} \frac{R^3}{m} \right) \frac{d^2 x}{dt^2}
\]

\( F_R(t) \) is the random force
Surfaces at the Nanoscale

- When materials are reduced to the nanoscale the main change is the very large increase in fraction of atoms that reside on the surface in comparison with the volume.
- Example of gold FCC crystal.
- In a 1 cm$^3$ gold cube there are ~ $5.9 \times 10^{22}$ atoms, and only ~ $2 \times 10^{-6}$% of the atoms are on the surface.
- Hence any defect in the surface, e.g., a missing surface atom does not affect the gold cube.
- In a 1 nm$^3$ gold cube there are 108 gold atoms where ~ 84 atoms (78%) reside on the surface.
- Therefore the properties of this 1 nm$^3$ gold cube is controlled by the surface.
- The chemical and physical properties of nanomaterials are strongly controlled by their surfaces.
High Surface to Volume Ratio

\[ \text{Ratio} = \frac{4\pi R^2}{4/3\pi R^3} \]

\[ \text{Ratio} = 3/R \]

This ratio is very big when R is very small.
Melting Temperature

It gets lower as a gold nanoparticle gets smaller because a higher percentage of atoms are on the surface. Surface atoms are not bound to each other the same way bulk atoms are.