Interaction and force measurements
Direct force measurements

**FIGURE 12.3** Measuring forces via (a) a spring (externally applied force $\propto$ spring displacement: $F_{\text{ext}} = K\Delta D$), and (b) a constant force ($F_{\text{ext}} = \text{constant}$). For the typical force-law or force-distance curves $F(D)$ shown, instabilities occur at the positions shown, manifested by an inward jump on the way in (on approach) and an outward jump on the way out (on separation). (a) These jump instabilities will occur only if the effective spring constant $K$ is lower than the maximum slope of the $F(D)$ curve. Thus, if the system is infinitely stiff ($K = \infty$) there will be no instabilities on approach or separation. In contrast, if a constant external force $+F$ is applied to one of the surfaces (b), $K$ is effectively zero, and jumps will occur to the upper equilibrium points at $e$ on approach, and out from $F_{\text{ad}}$ on separation. No equilibrium is possible at surface separations between the Jump in and Jump out points.
Table 12.1 Typical Length Scales and Magnitudes for Noncovalent Interactions and the Ten Most Common Techniques for Measuring Them

<table>
<thead>
<tr>
<th>Typical Parameters</th>
<th>Atomic (physical bonds, atoms and small molecules, submolecular groups)</th>
<th>Nanoscopic (macromolecules, nanoparticles, small aggregates)</th>
<th>Microscopic (small colloidal particles, vesicles, biological cells)</th>
<th>Macroscopic (large particles, flat surfaces)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle radius</td>
<td>0.1 nm</td>
<td>1 nm</td>
<td>1 μm</td>
<td>1 mm</td>
</tr>
<tr>
<td>Binding or adhesion energy</td>
<td>1 kT</td>
<td>10 kT</td>
<td>1000 kT</td>
<td>$10^{10}$ kT, $100 \text{ mL/m}^2$</td>
</tr>
<tr>
<td>Adhesion force or pressure</td>
<td>$10^{-11}$ N = 10 pN</td>
<td>$10^{-10}$ N = 100 pN</td>
<td>$10^{-7}$ N = 100 nN</td>
<td>$10^{-4}$ N = 100 μN $10^{8}$ N/m$^2 = 10^3$ atm</td>
</tr>
<tr>
<td>Range of interaction$^a$</td>
<td>0.2 nm</td>
<td>2 nm</td>
<td>20 nm</td>
<td>50 nm</td>
</tr>
</tbody>
</table>

**Suitable Experimental Techniques$^b$**

- Atomic Force Microscopy (AFM)
- Micro Cantilever (MC) with tip
- Optical Tweezers or Optical Trapping (OT)
- Micro Pipette Aspiration (MPA)$^c$
- Bio Force Probe (BFP)$^c$
- Total Internal Reflection Microscopy (TIRM)
- Reflectance Interference Contrast Microscopy (RICM)$^c$
- Surface Forces Apparatus (SFA)
- Osmotic Pressure (OP) or Osmotic Stress (OS)
- Shear Flow Detachment (SFD)$^c$

$^a$Range is here defined as the distance $D$ at which the interaction energy $W(D)$ is of the same order as the thermal energy $kT = 4 \times 10^{-21} \text{ J}$ at 25°C.

$^b$Some techniques can only be used to measure attractive (e.g., adhesion) forces, some only repulsive forces, and some can measure both.

$^c$The MPA, BFP, RICM and SFD techniques are devoted mainly to biological-type measurements—for example, between vesicles or living cells, described in Part III.

*Table adapted from Leckband and Israelachvili (2001).*
Surface forces apparatus (SFA)

Tabor and Winterton (1969)
Israelachvili and Tabor (1972, 1973)
Israelachvili and Adams, 1978
Israelachvili, 1987b

Two crossed-cylinders
Mica surfaces in air, vacuum, or liquid
Multiple Beam Interferometry (MBI) using “fringes of equal chromatic order” (FECO)
SFA measurement

**Figure 1.** Top: The cationic surfactant DEEDMAC used to make the supported bilayers in the SFA studies. Middle: The polymers PEG, polyDADMAC, and poly(allyl)amine used to study the repulsive electrostatic and attractive depletion forces between DEEDMAC bilayers. Bottom: Schematic of the supported bilayers and surface geometry in the SFA experiments.

**Figure 2.** Measured forces between DEEDMAC bilayers in various CaCl$_2$ solutions at pH 4. Solid lines are DLVO fits using the parameters given in Table 1.
Atomic force microscopy (AFM)

Related to profilometry
Scanning mode or tapping mode
AFM scans of surface topology

Figure 5. AFM scan of roughness on the surface of a glass slide within a typical 1 μm square. The histogram shows the distribution of elevations on the 2D image, and the line graph shows the profile of elevations along a horizontal line bisecting the 2D scan.

Figure 6. AFM scan of roughness on the surface of a glass slide, spin-coated with a 1 μm thick PS film, within a typical 1 μm square. The histogram shows the distribution of elevations on the 2D image, and the line graph shows the profile of elevations along a horizontal line bisecting the 2D scan.

Figure 7. AFM scan of the top surface of a PS sphere (courtesy of Robert Considine). The lateral scale is 1 μm/division, and the vertical scale is 1.5 μm/division. The larger asperities have a height of 40 nm.

Colloidal probe AFM

Fig. 1: Scanning electron micrograph of silanized silica microsphere glued to the end of a tipless atomic force microscope cantilever.

Total internal reflection microscopy (TIRM)

Prieve, 1999
Prieve and Frej, 1990
Prieve et al., 1990

\[
\rho(D) = A \exp \left[ - \frac{\phi(D)}{kT} \right]
\]

Interaction potential, \( W(D) \)

Density distribution, \( \rho(D) \)

\( D \) (nm)
TIRM measurement

\[ E(l) = -\frac{A_{132}(l)}{12\pi l^2} \quad (1) \]

\[ A_{132}(l) = \frac{3}{2} kT \sum_{n=0}^{\infty} \int_{r_n}^{\infty} \frac{x\left[\ln(1 - \Delta_{13}\Delta_{23}e^{-x}) + \ln(1 - \Delta_{13}\Delta_{23}e^{-x})\right]}{dx} \]

\[ \Delta_{jk} = \frac{\varepsilon_j s_k - \varepsilon_k s_j}{\varepsilon_j s_k + \varepsilon_k s_j} \quad \text{and} \quad \Delta_{k} = \frac{s_k - s_j}{s_k + s_j} \]

\[ s_k = x^2 + \left(\frac{2\xi_n l}{c}\right) (\varepsilon_k - \varepsilon) \]

\[ r_n = \frac{2|\xi_n|\sqrt{\varepsilon_2}}{c} \quad \varepsilon_k = \varepsilon_k (i\xi_n) \quad \xi_n = \frac{n kT}{h} \]

\[ \phi(h) = 2\pi a \int_{r}^{\infty} E(l) \, dl \quad (3) \]

\[ \phi(h) = -\frac{A(h)\left[2a + a - \ln\left(\frac{h + 2a}{h}\right)\right]}{6} \quad (4) \]

**Figure 1.** Profiles of the colloid interactions between the same 6 \( \mu \)m PS sphere and a glass slide in solutions having different ionic strengths. The solid line is an empirical fit given by eq 5, the dashed line shows the van der Waals interaction predicted from the Lifshitz–Derjaguin equation (eq 3), and the dot–dash line shows the van der Waals interaction predicted from the Lifshitz–Hamaker equation (eq 4).

Interaction measurements

**TIRM, surfactant micelles**


**TIRM, rigid rods**


**TIRM, polyelectrolytes**

Optical tweezers

Laser tweezer apparatus

Back focal plane detection
Measuring colloidal “stickiness”

A single bond rupture

Trap separation, $r_T$ ($\mu$m)

Displacement from trap, $\Delta x_s$ ($\mu$m)

Static trap

Moving trap

Repulsive

Attractive

$\Delta x_s = 0$

1 $\mu$m

t = 4.0 s

t = 11.1 s

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“Line tweezer” interaction measurements

Depletion attraction between flexible rods

Direct force measurements and interpretation

Measurements use curved interfaces
(sphere-flat, two spheres, crossed cylinders)

\[ W(D)_{\text{curved}} = -\int_{\infty}^{D} F(D)_{\text{curved}} dD \]

\[ W(D)_{\text{flat}} = \frac{F(D)_{\text{curved}}}{2\pi R} \quad \text{Derjaguin approximation} \]

\[ P(D)_{\text{flat}} = \frac{dW_{\text{flat}}}{dD} = \frac{dF(D)_{\text{curved}}}{2\pi R} \]
Direct force measurements and interpretation

FIGURE 12.4 Generic geometry for force-measuring techniques that employ springs, showing the relevant parameters that must be controlled and/or measured, preferably as a function of time $t$, during a force measurement: the force $F$, the undeformed surface radius $R$, the surface separation $D$, the spring deflection $\Delta D_0$, the force-measuring (cantilever) spring constant $K$ such that $F(D) = K\Delta D_0$, the effective stiffness of the material $K^*$ and its elastic deformation $\delta$ (see JKR theory in Chapter 17 and Figure 12.5), the flattened area $A = \pi a^2$ of the surfaces when in contact, and the film thicknesses $T_1$ and $T_2$. One can define a laboratory reference distance $D_0$ such as that when the base is moved the change in the surface separation $\Delta D$ is given by Eq. (12.6): $\Delta D = \Delta D_0 \pm \Delta D_\delta \pm \delta$. 

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Two oil droplets interacting


**Fig. 1.** (A) A schematic of the experiment between two oil droplets, one immobilized on the cantilever and the other immobilized on the substrate of an atomic force microscope. (B to D) The dynamic interaction force \( F \) versus piezo drive motion \( \Delta X \) between two decane droplets in aqueous solution in the presence of SDS at a series of approach (open symbols) and retract (filled symbols) velocities (green circles, 2 \( \mu \)m/s; blue triangles, 9.3 \( \mu \)m/s; red diamonds, 28 \( \mu \)m/s) over a range of SDS concentrations: (B) 0.1 mM, (C) 3 mM, and (D) 10 mM. The points refer to the experimental data, and the solid lines are the calculated force curves from a comprehensive model of the dynamic droplet interactions.
JKR apparatus

**Figure 12.5** A JKR apparatus named after the Johnston-Kendall-Roberts theory of adhesion mechanics (Johnson et al., 1971), developed by Tirrell and coworkers (Mangipudi et al., 1995; Tirrell, 1996) to study the adhesion forces and deformations of macroscopic solids. The device allows for the measurement of the molecular contact radius $a$ as a function of the applied load $F$, including negative loads. The results can then be used to test theories of adhesion and contact mechanics such as the JKR and Hertz theories (Chapter 17). This technique also enables the measurement of surface energies $\gamma$ via Eq. (11.17) or Eq. (12.10).
Adhesion between elastic particles
JKR Theory


\[ P_0 = 0 \quad a_c = \left[ \frac{3\pi a^2 W_{SL}}{2K} \right]^{1/3} \]

Surface adhesion energy:
\[ W_{SL} = \gamma_S + \gamma_L - \gamma_{SL} \]

\[ W_{SL} = \gamma_L (1 + \cos \theta_0) \approx 93 \text{mJ/m}^2 \]

where\(^1\) \[ \theta_0 = 73.7 \pm 0.3^\circ \]
\[ \gamma_L \approx 72 - 73 \text{mN/m} \]

Elastic modulus:
\[ K = \frac{2E}{3(1-\nu^2)} \]
\[ K \approx 2.5 \text{GPa}^2 \]

---

\(^1\) Kwok et al. J. Colloid Interface Sci. 206, 44 (1998).
\(^2\) Jarvis and Scheiman, J. Phys. Chem. 72, 74 (1968).
Instabilities

Constant volume (e.g. low vapor pressure)

$$D_c \approx \pi d \approx (4\pi V)^{1/3}$$

VL equilibrium

Continuous transitions

**FIGURE 12.6** The different geometries of liquid bridges can give rise to instabilities in the “capillary forces” measured on approach or separation of two surfaces. Shown here are the rapid mechanical instabilities and slower thermodynamic transitions that can occur on approach (a→b) and separation (b→c) of two surfaces with a liquid film on each. At (c) a mechanical instability (rapid snapping) occurs at a critical distance $D_c \propto V^{1/3}$, where $V$ is the (constant) volume of the liquid. At thermodynamic equilibrium (d and e), $V$ is no longer constant; instead, the mean curvature of the liquid-vapor interface is now constant and equal the Kelvin radius $r_K$ (Ch. 17). Some transitions in confined geometries and thin films can be slow and/or continuous rather than abrupt (Stroud et al., 2001).
Interaction measurements

**TIRM, surfactant micelles**

**TIRM, polyelectrolytes**

**Line tweezers, flexible rods**

**TIRM, rigid rods**
Optical micromanipulation

- Optical trap
- $\Delta x$
- $h$
- $r$
- $F_{12}(h)$
- $F_{\text{trap}}$
- $\kappa_t$
Radiation forces

Photon momentum \[ p = \hbar k \]
\[ |k| = 2\pi/\lambda \]

Radiation pressure acting on macroscopic surface
\[ P_{rad} \sim 2qI_0/c \]
\[ I_0 = 1000\text{W/m}^2 \]
\[ q = 0.1 \]
\[ \approx 10^{-8}\text{N/m}^2 \]

Radiation force exerted on micrometer diameter particle
Particle diameter \[ 2a = 1\mu m \]
Laser power \[ 10\text{mW} \]
\[ F_{rad} \approx 10^{-11}\text{N} \]
\[ kT/a \approx 10^{-14}\text{N} \]
\[ F_{rad} \sim 10^3 kT/a \]
Radiation forces in a Gaussian beam


Guassian beam

Collimated TEM$_{00}$

Ray $a$

Ray $b$

Resultant force imparted on particle

$p_{a,i}$, $p_{a,f}$, $p_{b,f}$, $p_{b,i}$

$\Delta p_a$, $\Delta p_b$
Focused Gaussian beam

$w_0 = \frac{\lambda}{2NA_0}$

$z_R = \frac{\pi n w_0^2}{\lambda}$

$NA_0 = n \sin \theta$

Diffraction limited beam width

Rayleigh length

Numerical aperture

$J. \ Mertz. \ Introduction \ to \ Optical \ Microscopy. \ Roberts, \ Greenwood \ Village, \ Colorado, \ 2010.$
Radiant field

\[ E(\rho, z) = E_0 \frac{w_0}{w(z)} e^{i2\pi \kappa z} e^{-\rho^2/w(z)^2} e^{i\pi \kappa \rho^2 / R(z)} e^{-i \eta(z)} \]

\[ w(z) = w_0 \sqrt{1 + z^2/z_R^2} \]

\[ R(z) = z \left(1 + z_R^2/z^2\right) \]

\[ \eta(z) = \tan^{-1}(z/z_R) \]

\[ \kappa = n/\lambda \]

Intensity (irradiance)

\[ I(\rho, z) = \langle E(\rho, z)E^*(\rho, z) \rangle \]

\[ [=] W/m^2 \]

Density plot of beam intensity
Typical values

- $\lambda_{\text{vacuum}} = 1064\text{nm}$
- $NA_0 = 1.1$
- $\theta = 58^\circ$
- $w_0 = 0.48\mu m$
- $z_R = 0.92\mu m$
- $2a = 3.0\mu m$

$\alpha > z_R$

Beam diverges with full angle

Analyze in ray-optic regime

$I(\rho, z) = \langle E(\rho, z)E^*(\rho, z) \rangle$
Gradient force trap


Ray optic regime

\[ d \gg \lambda \]

\[ \Delta p_a \]

\[ p_{a,in} \]

\[ p_{a,out} \]

High NA objective

\[ F_a \]

\[ F_b \]

\[ F_{\text{gradient}} \]
Gradient force trap

Ray optic regime

\[ d \gg \lambda \]
Lateral displacement

Ray optic regime

\[ d \gg \lambda \]
Rayleigh regime

$d \ll \lambda$

Induced dipole $\mathbf{p} = \alpha \mathbf{E}$

Energy and force $U = -\mathbf{p} \cdot \mathbf{E}$, $\mathbf{F} = \nabla (\mathbf{p} \cdot \mathbf{E})$

$\mathbf{F}_{\text{gradient}} = 2\pi \varepsilon \varepsilon_0 \mathcal{R}\{\alpha(\omega)\} a^3 \nabla \langle E(\rho, z)E^*(\rho, z) \rangle$

$\mathbf{F}_{\text{gradient}} = \frac{4\pi \varepsilon \varepsilon_0 a^3}{c} \left[ \frac{n_p^2 - n_s^2}{n_s (n_p^2 + 2n_s^2)} \right] \nabla I$

$\langle E(\rho, z)E^*(\rho, z) \rangle = \frac{2I(\rho, z)}{cn_s \varepsilon_0} = \left( \frac{2}{cn_s \varepsilon_0} \right) \left( \frac{I_0 e^{-2\rho^2/w(z)^2}}{1 + z^2/z_R^2} \right)$

$w(z) = w_0 \sqrt{1 + z^2/z_R^2}$
Important parameters for optical trapping

The ability to optically trap a particle depends on:

- The particle size and shape
- The refractive index contrast between the particle and medium
- The amount of light absorbed by the particle and sample
- The laser wavelength
- The laser power
- The quality of the beam and focus
- The laser mode (Gaussian, Laguerre-Gaussian, etc.)
“Steady drag” measurements

\[ F_{\text{drag}} = 6\pi a \eta U = \kappa_t \Delta x \]

\[ F_{\text{drag}} > F_{t,\text{max}} \]
Optical tweezer calibration

1 μm polystyrene, Nd:YAG (\(\lambda=1064\)nm)


**Trap stiffness**

\[ \kappa_T \sim a^3 \] Rayleigh regime

**Escape force**

Plateaus in ray-optic
Trap calibration—power spectral method

- Use power spectral density (PSD) from photodiode detector
- Fit corner frequency to find trap stiffness, $\alpha$
- Langevin equation
  $$\beta \ddot{y} + \alpha \dot{y} = F(t)$$
- PSD & corner frequency
  $$S_{yy} = \frac{kT}{2\pi\beta(f_0^2 + f^2)}$$
  $$f_0 = \alpha (2\pi \beta)^{-1}$$

Force calibration, 0.6$\mu$m silica particle

Adapted from K. Svoboda and S.M. Block, 1994.
Optical tweezer experiment

Laser tweezer apparatus

Back focal plane detection
Scattered light collected by condenser is imaged onto a quadrant photodiode

Spatial resolution ~ nm,

Frequency response ~ 10kHz

Source can be trap laser or co-aligned laser

  Fixed vs. moving reference frame

Can be extended to two independent beams by splitting polarization

Bandwidth improved using non-Si detectors

Rupturing “bonds” between colloids

Measuring thermal rupture forces

A single bond rupture

Static trap

Moving trap

\( c/c^* = 0 \)

\( c/c^* = 0.83 \)

\( \Delta x_s = 0 \)

\( t = 4.0 \text{ s} \)

\( t = 11.1 \text{ s} \)

\( t = 13.4 \text{ s} \)

\( t = 15.1 \text{ s} \)

\( t = 18.5 \text{ s} \)

1 \( \mu m \)

Displacement from trap, \( \Delta x_s (\mu m) \)

Time (s)
Repeated cycles
Multiple trajectories
Two state trajectory model

\[ \text{retraction} = \begin{cases} 
- r_T & \text{with } P(r_T) \\
\langle \text{approach} \rangle & \text{with } 1 - P(r_T)
\end{cases} \]

Probability of being bonded

\[ P(r_T) = \frac{\langle \text{retraction} \rangle - \langle \text{approach} \rangle}{(-r_T) - \langle \text{approach} \rangle} \]
Thermal rupture force distribution


- Probability of being bonded
- Rupture force distribution [pN⁻¹]
- Imposed force [pN]

PS microspheres in SDS
- 25 mM
- 35 mM
- 40 mM
- 50 mM

Increasing attraction
PMMA rupture distribution $c/c^* = 0.81$

Thermal model of bond rupture


\[ F = U(r) - f r \]

\[ r - 2a \]

\[ f = 0 \]

\[ f < f^* \]

\[ f = f^* \]

\[ \Delta F^\dagger \]

Mean first-passage time

\[ \frac{\partial P}{\partial t} = - \nabla \cdot \mathbf{D} \cdot \left[ (f - \nabla U)P/kT - \nabla P \right] \]

\[ \frac{1}{\tau_{\text{bond}}} = j_+ = D_r \left[ \left( f - \frac{dU}{dr} \right) \frac{P}{kT} - \frac{dP}{dr} \right] \]

\[ j_+ = -D_r \left[ \frac{dP}{dr} + \frac{dF(r)}{dr} \frac{P}{kT} \right] \]

\[ \tau_{\text{bond}} = \frac{1}{j_+} = \int_{2a}^{r^\dagger} e^{-F(r)/kT} \left[ \int_{r}^{r^\dagger} \frac{1}{D_r(y)} e^{F(y)/kT} dy \right] dr \]

\[ D_r = \frac{2k_B T(r - 2a)}{3\pi a^2 \eta} \]
Thermal model of bond rupture


\[ F = U(r) - fr \]

\[ r - 2a \]

\[ f = 0 \]

\[ f < f^* \]

\[ \Delta F^\dagger \]

\[ \mathcal{R} f f = f^* \]

\[ f^\dagger \]

\[ \tau_{\text{bond}} = \frac{1}{j_+} = \int_{2a}^{r^\dagger} e^{-F(r)/kT} \left[ \int_r^{r^\dagger} \frac{1}{D_r(y)} e^{F(y)/kT} dy \right] dr \]

Rate of bond rupture

\[ \frac{dS_1}{dt} \approx -j_+S_1 \]

Rate of loading

\[ r_f \frac{dS_1}{df} \approx -j_+S_1 \]

Cumulative bond probability distribution

\[ S_1(f) = \exp \left( -\frac{1}{r_f} \int_0^f j_+(f) df \right) \]
DLVO+AO interaction potential

PHSA-PMMA $2a = 2.7 \, \mu m$, $R_g = 32 \pm 2 \, nm$, Steric brush length $\delta = 7 \, nm$

$R_g = 32 \pm 2 \, nm$

PHSA brush cutoff, 7nm
Rupture force distribution calculated from theoretical AO potential


PHSA-PMMA $2a = 2.7$ μm, $R_g = 32 \pm 2$ nm, Steric brush length $\delta = 7$ nm

Calculated range for distribution

<table>
<thead>
<tr>
<th>$c/c^*$</th>
<th>Measured force distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>2.1 pN/s</td>
</tr>
<tr>
<td>0.46</td>
<td>2.4 pN/s</td>
</tr>
<tr>
<td>0.58</td>
<td>2.7 pN/s</td>
</tr>
<tr>
<td>0.69</td>
<td>3.2 pN/s</td>
</tr>
<tr>
<td>0.80</td>
<td>3.2 pN/s</td>
</tr>
<tr>
<td>0.93</td>
<td>3.9 pN/s</td>
</tr>
</tbody>
</table>
Rupture forces calculated from AO potential


PHSA-PMMA $2a = 2.7 \, \mu m$, $R_g = 32 \pm 2 \, nm$, Steric brush length $\delta = 7 \, nm$

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<td>3.5 pN/s</td>
</tr>
<tr>
<td>0.93</td>
<td>3.9 pN/s</td>
</tr>
</tbody>
</table>
Directed assembly of aggregates


Time shared and scanning optical traps

\[ \nu = \frac{2k_B T [\text{erf}^{-1}(\gamma)]^2}{3\pi a^3 b^2} \]


High bandwidth positioning using AOD Assembly in salt solutions

2X real-time

10 \mu m
Linear elastic behavior of aggregates


1.47μm PMMA, 11 particles, 250mM MgCl₂

3-point bending geometry

$$y - y_0 (μm) = -F EI (Lx^2_i - |x_i|^2/6)$$

Comparison to beam equation

Note: aggregates > 100μm from interface
Linear bending mechanics in MgCl₂

Aggregate rigidity displays surprising dependence on salt concentration


Rigidity

Scaling behavior

Open symbols: PS
Closed symbols: PMMA
Single bond bending rigidity

1.47μm PMMA

Salt conc. (mM) vs. κ₀ (N/m)

- NaCl
- CaCl₂
- MgCl₂
Typical colloidal interactions

DLVO-van der Waals + double layer

DLVO cannot account for tangential forces or salt dependence

Israelachvili, Intermolecular and Surface Forces
Bond rigidity

\[ I = \frac{\pi a_c^4}{4} \]

Area moment of inertia

\[ \kappa(L) = \kappa_0 \left( \frac{a}{L} \right)^3 \]

\[ = \frac{F_y}{y(L)} = \frac{3EI}{L^3} \]

\[ \kappa_0 = \frac{3EI}{a^3} \]

Bending rigidity in terms of contact radius
JKR Theory


\[ P_0 = 0 \quad a_c = \left[ \frac{3\pi a^2 W_{SL}}{2K} \right]^{1/3} \]

Surface adhesion energy:

\[ W_{SL} = \gamma_S + \gamma_L - \gamma_{SL} \]

\[ W_{SL} = \gamma_L (1 + \cos \theta_0) \approx 93 \text{mJ/m}^2 \]

where\(^1\) \( \theta_0 = 73.7 \pm 0.3^\circ \)

\[ \gamma_L \approx 72 - 73 \text{mN/m} \]

Elastic modulus:

\[ K = \frac{2E}{3(1 - \nu^2)} \]

\[ K \approx 2.5 \text{GPa} \]

\(^1\) Kwok et al. J. Colloid Interface Sci. 206, 44 (1998).

\(^2\) Jarvis and Scheiman, J. Phys. Chem. 72, 74 (1968).

Single-bond rigidity:

\[ \kappa_0 = \frac{3\pi E a_c^3}{a^3} = \frac{3\pi E}{4a^3} \left( \frac{3\pi a^2 W_{SL}}{2K} \right)^{4/3} \]

Relates mechanics to adhesion energy (particle interfacial phenomena)
Calculated bending rigidity

\[ \kappa_0^{\text{JKR}} = 82 \text{mN/m} \]

\[ a_c = 40 - 80 \text{nm} \]

Salt concentration (mM)

\[ \kappa_0 (\text{N/m}) \]

\[ 4 \times \text{higher due to Coulombic repulsion} \]

\[ \text{CaCl}_2 \quad \text{MgCl}_2 \quad \text{NaCl} \]
Divalent ion adsorption to PMMA

- Bond rigidity collapses with zeta potential
- Maximum at point of zero charge
- Calculate fractional coverage of divalent ion

\[ \theta = \frac{[C^{++}S^{-1}]}{[S] Tot} \]
Ion-bridge model

Total adhesion energy

\[ W_{SL} = W_{SL}^0 + W_{SL}^{ES} + W_{SL}^{\text{div}} \]

vdw  Coulomb  ion bridge

Divalent ions "bridge" charged adsorption sites

\[ W_{SL}^{\text{div}} \sim \theta (1 - \theta) \]

\[ W_{SL}^{ES} \sim -\left(\frac{\sigma}{e}\right)^2 \pi a_c^2 \]

\[ \sim -(1 - 2\theta)^2 \pi a_c^2 \]

\[ \kappa_0 = \frac{3\pi Ea_c^3}{a^3} = \frac{3\pi E}{4a^3} \left( \frac{3\pi a^2 W_{SL}}{2K} \right)^{4/3} \]
Ion bridge model


\[
W_{SL} = W_{SL}^0 + W_{SL}^{ES} + W_{SL}^{div}
\]

\[
\kappa_0 = \frac{3\pi E}{4a^3} \left( \frac{3\pi a^2 W_{SL}}{2K} \right)^{4/3}
\]

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Non-linear mechanics

Critical bending moment

\[ M_c = L^* F^* \]

New microscopic yielding mechanism
Yield stress due to critical moment

\[ \xi \sim a (\phi / \phi_e)^{3/(d_f-3)} \]

Maximum tensile force

\[ F_{\text{tens}} \sim \xi^2 \sigma_y \]

Maximum bending moment

\[ \Gamma \sim \xi^3 \sigma_y \]

Predicted yield stress

\[ \sigma_y^{\text{bend}} \sim M_c a^{-3} (\phi / \phi_e)^{3/(3-d_f)} \]

Predicted particle size dependence

\[ M_c \sim a^{4/3} \]

\[ \sigma_y^{\text{bend}} \sim a^{-5/3} \]
Comparison to bulk rheology

Bulk yield stress, PS latices

Expected from critical moment


If yield due to maximum tensile force, $\sigma_y \sim F_{tens} \xi^{-2} \approx 1\text{kPa}$