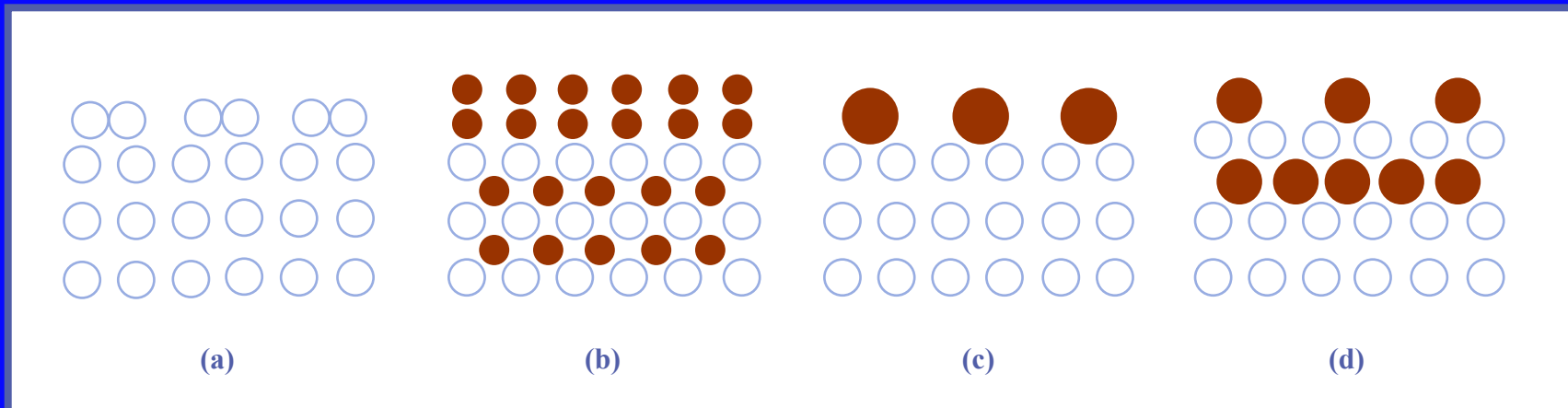# Chapter 2 Chemical and Physical State of the Solid Surface

Atomic Arrangement of the Solid Surface
(to lower the free energy of formation)

(a) reconstruction, (b) segregation, (c) chemisorption, (d) formation of compounds, (e) physisorption, (f) nucleation of atoms on the surface

(a)   (b)   (c)   (d)

Figure by MIT OCW. After Estrup, 1975.

Why is the state of the surface important in tribology?

1. **Light load**
   - **Important -- mechanical properties, surface contaminants, reconstruction of the surface, etc.**
   - **Contaminants -- adhesion**

2. **Heavy load**
   - **Less important**
   - **Elastic and plastic deformation dominated**

3. **Small contacts**
   - **Important**

4. **Large contacts**
   - **Less important**

Much progress due to the availability of instrumentation

1. Scanning electron microscope (SEM)
2. Atomic force microscope (AFM)
3. Auger spectroscope
4. Etc.

Modification of the surface through the use of coating techniques

1. Molecular beam epitaxy (MBE)
2. Chemical vapor deposition (CVD)
3. Physical vapor deposition (PVD)
4. Atomic layer deposition (ALD)
5. Diamond-Like Carbon or Coating (DLC)

General Characteristics of Metals

1. Metallic bonding
2. Structure -- fcc, bcc, hcp
3. Defects control mechanical properties.
   - Dislocations
   - Vacancies
4. Higher energy state at the surface -- Surface energy
5. Importance of microstructure
6. Alloys -- substitutional, interstitial, multiphase, dispersion strengthened,
7. Reactive -- oxides, carbides, intermetallics

General Characteristics of Polymers

1. Covalently bonded long chain molecules
2. Thermoplastics, thermosets, elastomers, liquid crystal polymers (LCD)
3. Linear polymers -- HDPE, PTFE
4. Semicrystalline vs amorphous polymers
5. Low melting point, glass transition temperature
6. Difference in molecular weight at the surface and the bulk = f(nucleation conditions)

General Characteristics of Ceramics

1. Mostly ionic bonding, some have covalent bonding
2. Combination of metallic and nonmetallic elements
3. Oxides and nitrides are very stable -- Low free energy of formation
4. Carbides are very hard and have very high temperature
5. Brittle
6. Electrically non-conducting
7. Abrasives

General Characteristics of Composites

1. Typically resin + fibers or filler or both
2. Fiber orientation important
3. May be designed to achieve specific properties
4. Used without lubricants

General Characteristics of a Solid Surface

1. Surface energy

2. Surface may be different from the bulk in atomic structure, mechanical properties, chemical state

Electric double layer
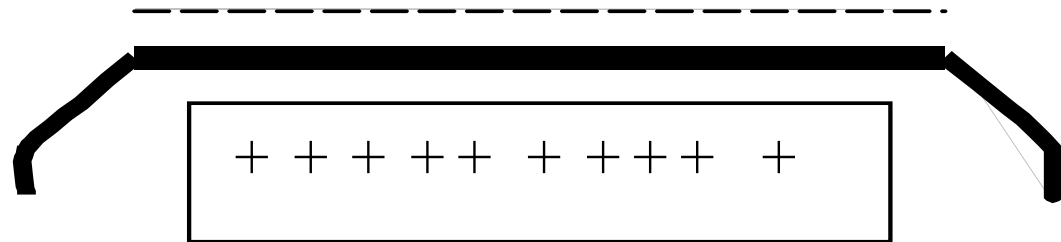
Role of lubricants

1. Change surface energy (monolayer)

2. Reduce metal to metal contact through wetting

3. Prevent particle agglomeration through wetting

Mechanical Properties of the Surface

1. Is the surface harder or softer than the bulk?

2. Does it matter?

Mechanical Properties of the Surface
(aluminum monocrystal – after Kramer and Demer, 1961
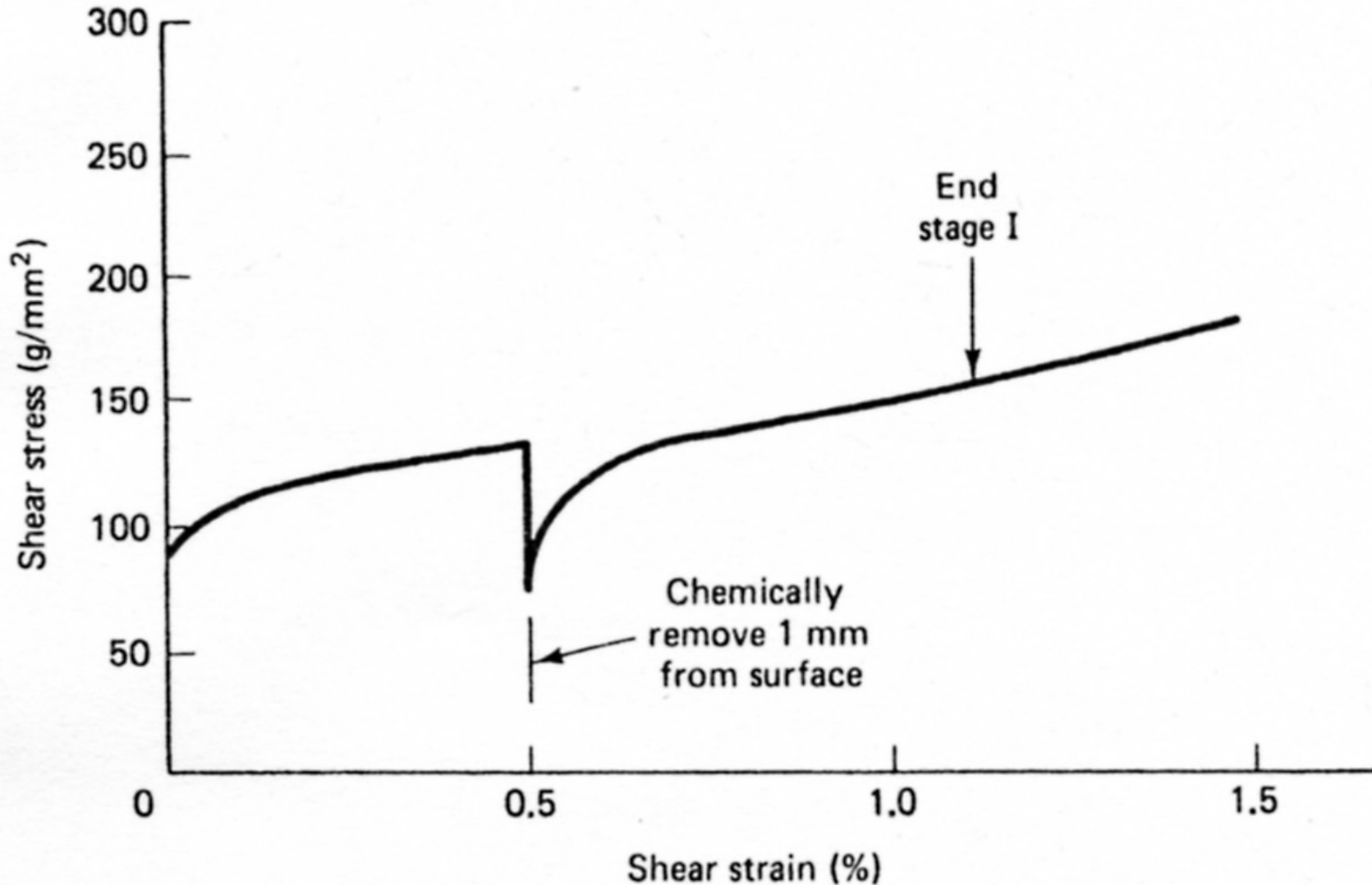
Mechanical Properties of the Surface
(Copper -- Fourie, 1968)

Graph removed for copyright reasons.
See Figure 2.3 in [Suh 1986]: Suh, N. P. *Tribophysics*. Englewood Cliffs NJ: Prentice-Hall, 1986. ISBN: 0139309837.

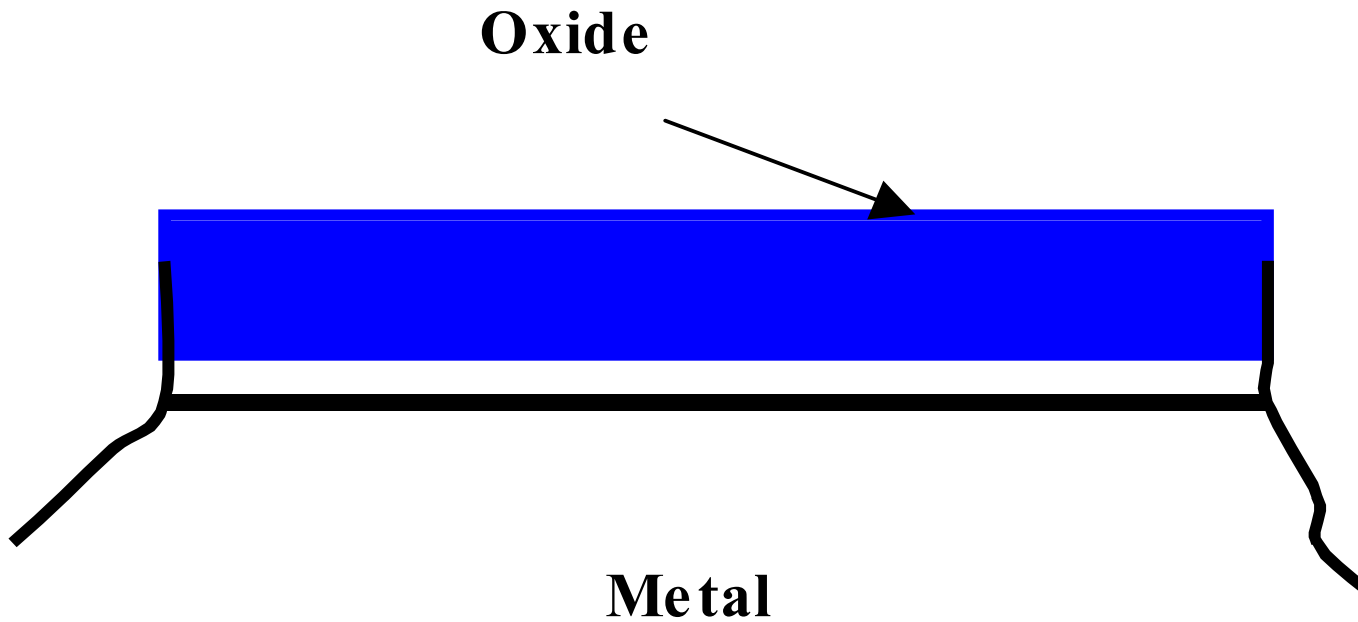# Image force on dislocations near the surface

1. Dislocations near the surface experience an image force due to the free surface

$$\tau_{i} = \frac{Gb}{4\pi(1-\nu)h}$$

$$h = \frac{Gb}{4\pi(1-\nu)\sigma_{i}}$$

Thermodynamic analysis of an Interface

Oxide

Metal

Thermodynamic analysis of an Interface

How thick is the interface?

$$f(c, \nabla c, \nabla^2, ...) = f_0(c) + \sum_{i} L_i \left(\frac{\partial c}{\partial x_i}\right) + \sum_{i,j} K_{i,j}^{(1)} \left(\frac{\partial^2 c}{\partial x_i \partial x_j}\right) + \frac{1}{2} \sum_{i,j} K_{i,j}^{(2)} \left(\frac{\partial c}{\partial x_i}\right) \left(\frac{\partial c}{\partial x_j}\right) + ...$$

Thermodynamic analysis of an Interface
Free energy of a binary system as a function of composition

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See Figure 2.6 in [Suh 1986]: Suh, N. P. *Tribophysics*. Englewood Cliffs NJ:
Prentice-Hall, 1986. ISBN: 0139309837.

Thermodynamic analysis of an Interface
Interfacial free energy as a function of composition
(from Cahn and Hilliard, 1958)

$$\sigma = N_v \int_{-\infty}^{\infty} \left[f_0(c) + K \left(\frac{dc}{dx}\right)^2 - c\mu_B(e) - (1-c)\mu_A(e) \right] dx$$

$$= N_v \int_{-\infty}^{\infty} \left[\Delta f_0(c) + K \left(\frac{dc}{dx}\right)^2 \right] dx$$