Microscopics

The ideal gas law,

$$PV = nRT = Nk_BT \qquad \qquad \frac{P}{k_BT} = \rho$$

is only an approximation. At low densities we have the "virial expansion",



Van der Waals Interactions

To simplify the situation, a coordinate change is made:

$$x_{\pm} = \frac{x_1 \pm x_2}{\sqrt{2}}$$
 $x_1 = \frac{x_+ + x_-}{\sqrt{2}}$ $x_2 = \frac{x_+ - x_-}{\sqrt{2}}$

$$\mathcal{H} = \frac{p_1^2}{2m} + \frac{1}{2} \left(m\omega_0^2 - \frac{2e^2}{R^3} \right) x_+^2 + \frac{p_2^2}{2m} + \frac{1}{2} \left(m\omega_0^2 + \frac{2e^2}{R^3} \right) x_-^2$$

The two terms in parenthesis are essentially adjusted frequencies:

$$\omega_{+}^{2} = \omega_{0}^{2} - \frac{2e^{2}}{mR^{3}} \qquad \qquad \omega_{-}^{2} = \omega_{0}^{2} + \frac{2e^{2}}{mR^{3}}$$

Van der Waals Interactions - continued

$$\omega_{\pm} = \left(\omega_0^2 \mp \frac{2e^2}{mR^3}\right)^{1/2} \simeq \omega_0 \mp \frac{e^2}{m\omega_0 R^3} - \frac{1}{2} \frac{e^4}{m^2 \omega_0^3 R^6} + \cdots$$

The energy is then:

$$U(r) = \frac{1}{2}\hbar\omega_{+} + \frac{1}{2}\hbar\omega_{-} - 2 \cdot \frac{1}{2}\hbar\omega_{0}$$
$$\approx \frac{-\hbar e^{4}}{2m^{2}\omega_{0}^{2}R^{6}} = -\frac{1}{2}\hbar\omega_{0}\frac{(e^{2}/m\omega_{0}^{2})^{2}}{R^{6}}$$

We see that $e^2/m\omega_0^2$ is a characteristic volume. To see the meaning of this, consider an induced electric dipole:

$$\mathbf{d} = \alpha \mathbf{E}$$

The units of **d** are $Q \cdot L$, the units of **E** are Q/L^2 , so the units of α are L^3 (a volume).

Van der Waals Interactions - continued

Now consider the Hamiltonian in the presence of an external electric field:

$$\mathcal{H} = \mathcal{H}_0 + eE_0 x_1 + eE_0 x_2$$

= $\frac{1}{2} m \omega_0^2 \left(x_1^2 + \frac{2eE_0 x_1}{m \omega_0^2} \pm \left(\frac{eE_0}{m \omega_0^2} \right)^2 \right) + (1 \leftrightarrow 2)$
= $\frac{1}{2} m \omega_0^2 z_1^2 + \cdots$
 $z_{1,2} = x_{1,2} + \frac{eE_0}{m \omega_0^2}$

This is nothing but a shifted pair of harmonic oscillators, and from the shift we deduce the polarizability The dipole moment is then:

$$\alpha = \frac{e^2}{m\omega_0^2}$$

which is the same as seen previously. The energy of attraction in either case is then:

$$U(r) = -\frac{1}{2} \frac{\hbar\omega_0 \alpha^2}{r^6}$$

How Does This Fit into the Thermodynamics?

Key idea [van der Waals, Weeks-Chandler-Anderson (WCA)]: partition the intermolecular potential into purely repulsive + purely attractive, use "known" results for former, perturbation theory for latter.

Using a mean-field (averaging) argument, contribution to the internal energy $U_{\text{attr}} = \frac{1}{2}N\rho \int d^3r u_{\text{attr}}(r)$ taking the density to be uniform $Define \quad a = -\frac{1}{2}\int d^3r u_{\text{attr}}(r) \quad \text{then} \quad U_{\text{attr}} = -aN\rho = -\frac{aN^2}{V}$

and
$$p_{\text{attr}} = -\frac{\partial U_{\text{attr}}}{\partial V} = -a\rho^2$$

So, a better equation of state is $p = \rho k_B T - a \rho^2$

To incorporate excluded volume, subtract Nb from the available volume, where $b = 8 \times \text{particle volume}$,

$$(p+a\rho^2)(V-Nb) = Nk_BT$$

Putting it All Together

Finally, we have

$$p = \frac{\rho k_B T}{1 - b\rho} - a\rho^2$$
 so $\frac{p}{k_B T} \simeq \rho + \left(b - \frac{a}{k_B T}\right)\rho^2 + \cdots$

and we conclude that



Applications of Dispersion Forces



Suppose the interaction between two molecules is

$$V_{11}(r) = -\frac{C}{r^6}$$

Then, the attraction between a neutral atom and a sheet is calculated:

$$V_{1S}(h) = \int_{h}^{\infty} dz \int_{0}^{2\pi} d\phi \int_{0}^{\infty} r dr \rho V_{11}(\sqrt{z^{2} + r^{2}}) = -\int_{h}^{\infty} dz \int_{0}^{2\pi} d\phi \int_{0}^{\infty} r dr \rho \frac{C}{(z^{2} + r^{2})^{3}} = -\frac{\pi C \rho}{6h^{3}} \quad \text{(atom-slab)}$$

Applications of Dispersion Forces - continued

Between two slabs of area A such that $A\rho dz$ atoms are in thickness dz:

$$V_{SS}(r) = A \int_{h}^{\infty} \rho V_{1S}(z) dz \Rightarrow \frac{V_{ss}}{A} = -\frac{A_H}{12\pi} \frac{1}{h^2}$$

This defines the Hamaker constant A_H

$$A_H = \pi^2 \rho_1 \rho_2 C_{12} \sim \pi^2 \hbar \omega (\alpha \rho)^2$$

Typically, the Hamaker constant is $\sim 5x10^{-20}$ J $\sim 5x10^{-13}$ erg, About an order of magnitude larger than thermal energy

$$A_H \sim \pi^2 \hbar \omega_0 (\alpha \rho)^2 \sim 10 \cdot \text{eV} \cdot (0.1)^2 \sim 0.1 \text{eV}$$

DLVO Theory



However, the dielectric constant $\epsilon \sim 80$, so even apart from screening the energy is reduced to $e^2/\epsilon r$. Turning this around, we define the *Bjerrum length* λ_B as the point of balance:

$$\lambda_B = \frac{e^2}{\epsilon k_B T} \sim 7 \mathring{A}$$

Screened Interactions

There are two basic ingredients in the calculation of screened electrostatic interactions (in the so-called Poisson-Boltzmann theory). 1. The Poisson equation relating the electrostatic potential ϕ to the charge density ρ :

$$\nabla^2 \phi = -\frac{4\pi\rho}{\epsilon} \qquad \mathbf{E} = -\nabla\phi$$

2. The Boltzmann distribution, relating the ionic concentrations c_s of the species s of valence z_s to the electrostatic potential

$$c_s = c_0 e^{-z_s e\phi/k_B T}$$

Combining these into a single self-consistent equation (with $\beta = 1/k_B T$), we obtain the *Poisson-Boltzmann equation*:

$$\nabla^2 \phi = -\frac{4\pi}{\epsilon} \sum_{species \ s} z_s e c_0 e^{-\beta z_s e \phi}$$

Screened Interactions - continued

If we consider the specific case of a z : z electrolyte (1:1, NaCl, 2:2, CuSO₄ etc.), we can write this in a more compact form:

$$\nabla^2 \phi = \frac{8\pi z e c_0}{\epsilon} \sinh(\beta z e \phi)$$

In the weak field limit, when $\beta e \phi \ll 1$, we can linearize the PB equation (using $\sinh(x) \simeq x + \cdots$):

$$\nabla^2 \phi = \frac{8\pi z^2 e^2 c_0}{\epsilon k_B T} \phi + \dots$$

This suggests a characteristic length scale, the Debye-Huckel length λ_{DH} :

$$\lambda_{DH} = \left[\frac{\epsilon k_B T}{8\pi z^2 e^2 c_0}\right]^{1/2} \sim \frac{10 \text{ nm}}{\sqrt{c_0[\text{mM}]}}$$

This finally shows that the Debye-Huckel limit is governed by the modified Helmholtz equation

$$\left(\nabla^2 - \lambda_{DH}^{-2}\right)\phi = 0$$

Screened Interactions - continued

The most elementary situation to consider is the one-dimensional problem of a surface held at fixed potential ϕ_0 , bounded by a semi-infinite electrolyte. The relevant solution of

$$\left(\frac{\partial^2}{\partial x^2} - \lambda_{DH}^{-2}\right)\phi = 0$$
 is $\phi = \phi_0 e^{-x/\lambda_{DH}}$

There is an induced charge density σ on the surface which can be computed in the usual way (Gaussian pillbox):

$$-\hat{\mathbf{n}} \cdot \nabla \phi|_{\text{surf}} = \frac{4\pi\sigma}{\epsilon} \Rightarrow \sigma_0 = \frac{\epsilon}{4\pi\lambda_{DH}}\phi_0$$

Once we have the potential everywhere and the charge on the surface we should be able to find the (free) energy of the system. Observe that $\nabla^2 \phi - \lambda_{DH}^{-2} \phi = 0$ is the Euler-Lagrange equation for the functional:

$$\tilde{\mathcal{F}} = \frac{\epsilon}{4\pi} \int d^3r \left[\frac{1}{2} (\nabla \phi)^2 + \frac{1}{2} \lambda_{DH}^{-2} \phi^2 \right]$$

Screened Interactions - continued

This was obtained with the general Euler-Lagrange formula

$$\frac{\delta \tilde{\mathcal{F}}}{\delta \phi} = -\frac{\partial}{\partial x} \frac{\partial (\cdots)}{\partial \phi_x} + \frac{\partial (\cdots)}{\partial \phi}$$

where (\cdots) is the integrand of the functional.

Now, here's the crucial point. If we take the original free energy and integrate by parts the term involving $(\nabla \phi)^2$, we obtain a surface term and a new bulk contributiion,

$$\tilde{\mathcal{F}} = \frac{\epsilon}{8\pi} \int_{S} dS \phi \hat{\mathbf{n}} \cdot \nabla \phi - \frac{\epsilon}{8\pi} \int d^{3}r \phi \left(\nabla^{2} \phi - \lambda_{DH}^{-2} \phi \right) = \frac{1}{2} \int_{S} dS \sigma \phi,$$

where σ is the surface charge. The bulk term vanishes by the DH equation (!).

For situations with fixed surface potential rather than fixed charge, the surface free energy must be Legendre transformed:

$$\mathcal{F} = \tilde{\mathcal{F}} - \int_{S} dS \sigma \phi = -\frac{1}{2} \int_{S} dS \sigma \phi \quad \text{or} \quad -\int_{S} dS \int^{\phi_{0}} \sigma(\phi') d\phi'$$

Interaction of Two Surfaces – Fixed Potentials

For fixed potential ϕ_0 on each surface, the solution of the DH equation is ϕ_0 ϕ_0 ϕ_0 ϕ_0 ϕ_0 The induced charge density is ϕ_0 $\sigma(d/2) = \frac{\varepsilon}{4\pi} \frac{\phi_0}{\lambda} \tanh(d/2\lambda)$

$$\frac{\mathcal{F}}{2A} = -\frac{1}{2} \int dS \sigma \phi = -\frac{\epsilon \phi_0^2}{8\pi \lambda} \tanh(d/2\lambda)$$

And the interesting quantity is the difference between this and the energy at infinite separation:

$$\frac{\mathcal{F}(d) - \mathcal{F}(\infty)}{2A} = \frac{\epsilon \phi_0^2}{8\pi \lambda_{DH}} \left[1 - \tanh\left(\frac{d}{2\lambda_{DH}}\right) \right]$$

Interaction of Two Surfaces – Fixed Charge



And the interaction energy per unit area is

$$\frac{\tilde{\mathcal{F}}(d) - \tilde{\mathcal{F}}(\infty)}{2A} = \frac{2\pi\sigma_0^2\lambda_{DH}}{\epsilon} \left[\coth\left(\frac{d}{2\lambda_{DH}}\right) - 1 \right]$$