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SPRING COLLEGE ON AMORPHOUS SOLIDS
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LIQUID SURFACES AND LIQUID-SOLID INTERFACES

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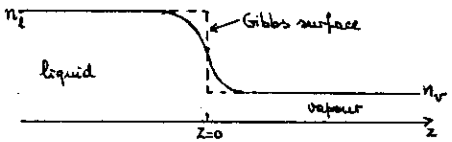
1. Thermodynamics of interfaces

1.1 Liquid-vapour interface

We consider for simplicity a monatomic liquid in equilibrium with its vapour, assuming a planar interface (perpendicular to the z axis, say). We expect that the atomic density $n(z)$ will vary continuously, over a distance of a few interatomic spacings (at least far from the critical point), from the value n_ℓ of the bulk liquid to the value n_v of the bulk vapour (see sketch). The system (N atoms in a total volume V, with N and V tending to infinity) is in thermodynamic equilibrium if the temperature T and the chemical potential μ are constant. Mechanical equilibrium of the surface requires that the normal pressure P_n be constant (equal to the pressure P in the two bulk phases).



The density profile $n(z)$ is a basic microscopic property of the planar liquid surface. From its qualitative shape we expect an anisotropy of the internal forces acting on an atom in the transition region, resulting in a net attraction to the liquid phase. One must therefore do work against the interatomic forces to bring an atom from the bulk of the liquid to the surface: namely, an excess of free energy is associated with the creation of the interface (surface free energy). There also follows that the tangential pressure (defined as the force per unit area perpendicularly transmitted across an area element in the y-z plane at height z) becomes a function $P_t(z)$ in the transition region. The components P_n ($=P$) and P_t of the stress tensor, which are equal in the bulk phases, differ from each other in the transition region: this is the origin of surface tension.

In order to define the excess free energy we must compare the real system with a hypothetical system constituted of homogeneous liquid and homogeneous vapour, separated by a plane (the Gibbs surface, that we can locate at $z=0$). Let V_ℓ and V_v be the volumes of such homogeneous fluids: these are determined by the relations

$$V_\ell + V_v = V \;, \qquad n_\ell V_\ell + n_v V_v = N \;. \tag{1}$$

These can also be expressed as

$$\int_{-\infty}^{0} dz \left[n_\ell - n(z) \right] + \int_{0}^{\infty} dz \left[n_v - n(z) \right] = 0 \,, \tag{2}$$

a relation which fixes the location of the Gibbs surface in such a manner that the excess density of matter is zero. We can now proceed to introduce the excess free energy γ per unit area (the surface free energy, or more precisely the liquid-vapour interfacial free energy $\gamma_{\ell v}$) by writing

$$\gamma = \frac{1}{A} \left[F - f_\ell V_\ell - f_v V_v \right] \tag{3}$$

where A is the area of the surface, F is the total free energy of the real system, and f_ℓ, f_v are the free energies per unit volume of the homogeneous phases.

From the above thermodynamic definition of γ the following thermodynamic results ensue:

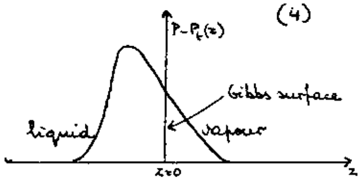
(i) $\gamma\, dA$ is the work [redacted] needed to increase in any isothermal reversible process the surface area by the amount dA (in particular, the work done against the surface tension in expanding the interface area is equal to the surface free energy of the same area of new interface: i.e. the surface tension and the surface free energy, commonly expressed in dyn/cm and in erg/cm² respectively, are numerically equal for an interface between two fluids[†]);

(ii) the excess surface entropy is given by $s = -d\gamma/dT$ per unit area, and hence the excess surface energy is $u = \gamma - T\frac{d\gamma}{dT}$ per unit area.

It is also easy to show (see Appendix 1) that γ is related to the integrated deficit of tangential pressure,

$$\gamma = \int_{-\infty}^{\infty} dz \left[P - P_t(z) \right] . \tag{4}$$

Since γ must be positive definite (otherwise the surface area would tend to increase spontaneously), $P_t(z) - P$ has the character of a tension (see sketch).



For a discussion of the position and thickness of the interface in multicomponent systems, see Cahn and Hilliard[1].

1.2 Empirical relations

Various empirical relations are known between the surface tension and physical properties of the bulk liquid. As a first example we report in the adjoining figure the correlation which exists between the values of γ for liquid metals near freezing and their latent heat of vaporization (from Faber[2]). This correlation

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[†] This is not necessarily true for an interface involving a solid: the surface free energy corresponds to the work done in forming the surface whereas the surface tension corresponds to the work done in stretching the surface. These two processes are equivalent only if they lead to the same surface structure – in practice if the temperature is sufficiently high for diffusion to correct distortions from the equilibrium structure.

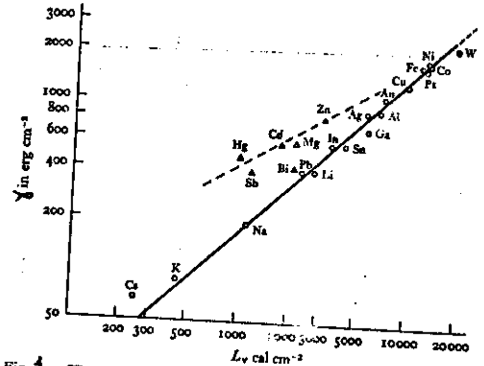


Fig. 1a. The surface tension of liquid metals at the melting point compared with the latent heat of vaporisation. (Redrawn by permission from Grosse (1964), *J. Inorg. Nucl. Chem.* 26, 1349.)

expresses the fact that the work done in bringing an atom from the bulk liquid up to the surface involves the breaking of a certain fraction (roughly half) of its interatomic bonds with its neighbours.

An empirical relation between γ and the isothermal compressibility K of the liquid is known to exist for a large variety of liquids, quite independently of their type of bonding: this is illustrated in the adjoining table (abridged from Egelstaff and Widom[3]) for several liquids near their triple point. The relation can be written

$$\gamma K = L \qquad (5)$$

where L has the dimensions of a length and is roughly constant (variations by a factor $2 \div 3$ only, whereas K and γ vary individually by a factor 10^2).

	γ (dyn/cm)	K (10^{-12} cm^2/dyn)	γK (Å)
Na	194	21	0.40
Cs	71	67	0.47
Cd	666	3.2	0.21
Fe	1790	1.43	0.25
NaCl	116	29	0.34
KI	78	50	0.39
Ar	13.1	212	0.28
N_2	11.8	211	0.25
Br_2	41.5	63	0.26

The interpretation of the relation (5) given by Cahn and Hilliard[1] (see also Widom[4]) is of considerable importance as an introduction to modern statistical-mechanical theories of the liquid surface, that we shall discuss in lecture 2. The main conceptual point is that one can still use a "bulk-like" theory in the presence of a surface provided that one keeps account of the gradient of the density profile. Cahn and Hilliard consider two contributions to γ. For the first, they notice that the free energy change associated with a density fluctuation δn in a volume v of a bulk liquid is

$$F_1 = c_1 v \left(\frac{\delta n}{n_\ell}\right)^2 / K$$

where c_1 is a proportionality constant ($c_1 = 1/2$ in elasticity theory). They use this formula for the surface by interpreting δn as the density change $n_\ell - n_v$ between liquid and vapour, but add to it a contribution F_2 specifically associated with the density gradient, writing it as

$$F_2 = c_2 v (\delta n / L)^2$$

where c_2 is another proportionality constant and L measures the distance over which $n(x)$ changes from n_ℓ to n_v. With $v = LA$ the expression for the surface tension is

$$\gamma = L (n_\ell - n_v)^2 \left[\frac{c_1}{K n_\ell^2} + \frac{c_2}{L^2}\right]$$

which upon minimization with respect to L yields

$$\gamma = \frac{2 c_1 L}{K} \left(\frac{n_\ell - n_v}{n_\ell}\right)^2 \simeq L/K \quad , \qquad (6)$$

near the triple point where $n_\ell \gg n_v$. Thus the product γK is a measure of the "thickness of the interface" L. We shall return again on this relation.

An interesting extension of this line of reasoning to the dependence of γ on concentration in liquid alloys has been given by Bhatia and March[5]. It is clear thermodynamically that the solute will tend to segregate in the surface region if γ decreases with increasing concentration c: namely surface segregation is related to the sign of $d\gamma/dc$. In the limit $c \to 0$ Bhatia and March find

$$\gamma \simeq \frac{L}{K} \left[1 + \frac{c\,\delta^2}{n_\ell k_B T K}\right]^{-1} \qquad (7)$$

namely

$$\left.\frac{d\ln\gamma}{dc}\right|_{c\to 0} \simeq \frac{d\ln L}{dc} - \frac{d\ln K}{dc} - \frac{\delta^2}{n_\ell k_B T K} . \qquad (7')$$

Here the quantity $\delta \equiv (\partial \ln V / \partial c)_{T,P,N}$ measures the difference of atomic sizes between solvent and solute, and obviously this effect always favours surface segregation (irrespectively of the sign of δ). The size effect is strengthened if $d\ln K/dc > 0$, i.e. if the compressibility of the solute is larger than that of the solvent. The original work[5] should be consulted for an analysis of experimental data: here we only wish to recall the drastic effect of surface segregation in amalgams of mercury with alkali metals.

We conclude this section by recalling that an approximate "law of corresponding states" is also known for the surface tension of simple atomic and molecular fluids: this is illustrated in the adjoining table

TABLE 1. VALUES OF $\gamma_R = V_c^{2/3} T_c^{-1} \gamma(T)$ AT $T = 0.56\ T_c$
(From Buff and Lovett (1968))

Substance	γ (dyne·cm^{-1})	γ_R (erg / K mole$^{-2/3}$)	γ_R/γ_R (Ar)
Ne	5.55	1.500	0.955
CH_4	13.790	1.548	0.986
Kr	16.081	1.568	1.000
Ar	13.28	1.570	1.000
Xe	18.98	1.583	1.008
O_2	14.04	1.605	1.022
N_2	10.42	1.662	0.059
CO	11.03	1.704	1.085

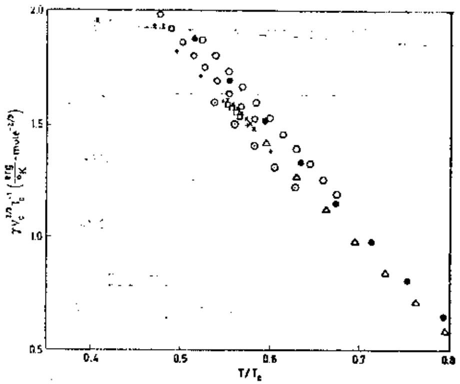


FIG. 2. $\gamma(T)\, V_c^{2/3}\, T_c^{-1}$ plotted versus T/T_c. ⊙: neon; △: argon; ×: krypton; □: xenon; ●: nitrogen; ⬭: carbon monoxide; +: methane; ○: oxygen. (From Buff and Lovett (1968).)

and figure• (from Buff and Lovett[6]). These show that the "reduced surface tension" γ_R, defined by

$$\gamma_R \equiv \gamma(T)\, v_c^{2/3} / k_B T_c \qquad (8)$$

where v_c is the critical volume per molecule and T_c is the critical temperature, is approximately a universal function of T/T_c for such molecular fluids. The experimental data are described by the empirical relation

$$\gamma(T) = \gamma_0 \left(1 - T/T_c\right)^{1.27 \pm 0.02} \qquad (9)$$

We expect in general that $\gamma(T)$ should decrease with increasing temperature (see § 1.3 below, where some exceptions are also noted) and vanish at the critical point where the distinction between liquid and vapour disappears. The corresponding "critical exponent" seems generally to be somewhat greater than unity.

1.3 Surface entropy

We have already noted in § 1.1 that the excess surface entropy is directly related to the temperature dependence of the surface tension, $s = -d\gamma/dT$. It seems intuitively clear that the entropy per surface atom should be intermediate between the entropies s_ℓ in the liquid and s_v in the vapour: since $s_v > s_\ell$, we expect a positive excess surface entropy and hence $d\gamma/dT < 0$.

Faber[2] has estimated s for liquid metals near freezing by noticing that a certain number of bulk modes must be replaced in a semi-infinite liquid by an equivalent number of surface modes. These are surface "ripple modes"

with a dispersion relation $\omega^2 = \gamma k^3/m n_\ell$ at long wavelengths and hence a density of states $N(\omega) = \frac{1}{3\pi}\left(\frac{m n_\ell}{\gamma}\right)^{2/3} \omega^{1/3}$ per unit area at [redacted] low frequencies. Using a 2-dimensional analogue of the Debye model Faber finds

$$-\frac{d\gamma}{dT} = k_B \left\{ \ln \frac{\Theta_D}{\Theta_S} + \frac{5}{12} \right\} \quad \text{per surface atom} \qquad (10)$$

where Θ_D is the bulk Debye temperature and Θ_S is the "surface Debye temperature", determined from the total number of surface modes as

$$\Theta_S = \frac{\hbar}{k_B} \left(\frac{4\pi}{1.09}\right)^{3/4} \left(\frac{\gamma}{m}\right)^{1/2}. \qquad (11)$$

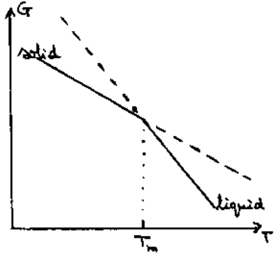
This estimate leads to $\Theta_D / \Theta_S \approx 1.8$ and hence $s \approx k_B$ per surface atom, in accord with the measured values of $d\gamma/dT$ for many liquid metals.

Some liquid metals (Zn, Cu and Cd in particular) seem however to be exceptions to this rule: their surface tension increases initially with temperature in the liquid state and starts decreasing only at a few hundred degrees above the triple point. Although the precise magnitude of $d\gamma/dT$ has been questioned, recent measurements have confirmed that $d\gamma/dT > 0$ for Zn near the triple point. It thus seems that in some systems the degree of order in the first few surface layers may be higher than in the bulk of the liquid. A possibly related peculiarity of these metals is that their drops solidify in faceted forms: marked density oscillations at the liquid surface could assist nucleation during solidification.

1.4 Solid-liquid interfacial free energy

An interface between a solid and its own liquid constitutes a much less severe perturbation of the homogeneous state, because the densities and coordinations of these two phases are usually quite similar. The excess free energy $\gamma_{s\ell}$ associated with this interface plays an important role in the process of solidification, and indeed its measurement for metals and many other materials is based on the method of determining the critical supercooling for homogeneous nucleation of the solid inside the melt. The plot of the Gibbs free energies of the two bulk phases in the neighbourhood of the melting point T_m is as sketched: at the phase transition there is a discontinuity in slopes, related to the latent heat of fusion ΔH_f by

$$\left(\frac{\partial G_s}{\partial T}\right)_p - \left(\frac{\partial G_\ell}{\partial T}\right)_p = \Delta H_f / T_m . \qquad (12)$$



Although the solid phase is the absolutely stable one below T_m, the possibility of supercooling the liquid arises from the fact that a finite amount of interfacial free energy is to be provided for the creation of the solid-liquid interface between a solid nucleus and the surrounding liquid.

Let us consider a spherical solid particle of radius r in a bulk liquid, at a temperature ΔT below T_m $(\Delta T = T_m - T)$: assuming that the slopes of G in eqn (12) do not vary appreciably over a moderate temperature range, the volume free energy of the solid particle relative to the surrounding liquid is $-\frac{4\pi}{3} r^3 \frac{\Delta H_f}{T_m} \Delta T$ while the interfacial free energy is $4\pi r^2 \gamma_{s\ell}$. Therefore the excess free energy of the solid nucleus is

$$\Delta G = -\frac{4\pi}{3} r^3 \frac{\Delta H_f}{T_m} \Delta T + 4\pi r^2 \gamma_{s\ell} \quad . \qquad (13)$$

This increases initially with r, to reach a maximum for $r = r^*$ where

$$r^* = \frac{2\gamma_{s\ell} T_m}{\Delta H_f \Delta T} \quad . \qquad (14)$$

The radius r^* gives for given ΔT the critical size of a solid nucleus beyond which it will grow spontaneously at the expense of the liquid phase with a release of free energy. Conversely we may look on eqn (14), rewritten as

$$\Delta T = \frac{2\gamma_{s\ell} T_m}{r^* \Delta H_f} \quad , \qquad (14')$$

as saying that (in the absence of heterogeneous nucleation processes at impurities or surfaces) the liquid can be supercooled until it reaches a temperature at which the size of the critical nucleus corresponding to that supercooling is such that there is an appreciable probability that such a nucleus will form out of random fluctuations of the atoms in the liquid.

The "nucleation transition" is in fact observed to be very sharp, and measurements of the maximum supercooling to which a liquid can be subjected before homogeneous nucleation occurs allow an estimation of $\gamma_{s\ell}$ (or more precisely of some unspecified average of this quantity over various crystalline planes). This quantity for metals is about 10% of the corresponding liquid-vapour interfacial free energy, and is found to correlate rather well with ΔH_f (Turnbull[7], see adjoining figure).

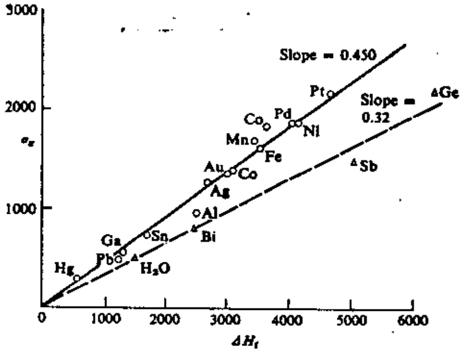
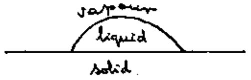
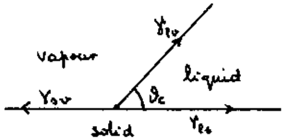


Fig. 2.10. Experimental values of the gram-atomic interfacial free energy σ_g versus latent heat of fusion (after Turnbull, 1950b).

1.5 Interface intersections

One of the most general methods of measuring the surface tension of an interface involves the study of the configuration that it adopts where it intersects some other interface. Consider for example in the sketch a sessile liquid drop on a solid, whose enlarged view below introduces the contact angle ϑ_c (measured through the liquid perpendicularly to the three-phase contact line). The equilibrium of the horizontal components of the surface-tension forces[+] yields





$$\gamma_{\ell v} \cos\vartheta_c + \gamma_{\ell s} = \gamma_{sv} \quad , \qquad (15)$$

which allows a determination of the relative values of the interfacial tensions from a measurement of the contact angle. The case that we have considered $(\vartheta_c < \pi/2)$ is conventionally called a "wetting" situation, to be contrasted with the case $\vartheta_c > \frac{\pi}{2}$ (non-wetting) and with a "spreading" situation where the liquid covers the whole solid surface.

Defining the "work of adhesion" W_a as

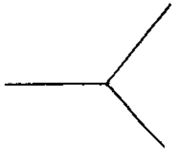
$$W_a = \gamma_{sv} + \gamma_{\ell v} - \gamma_{\ell s} \qquad (16)$$

(a positive quantity giving the work per unit area to pull the liquid away from the solid), we get from (15)

$$\frac{1}{2}(1 + \cos\vartheta_c) = \cos^2\left(\tfrac{1}{2}\vartheta_c\right) = \frac{W_a}{2\gamma_{\ell v}} \quad . \qquad (17)$$

The order of magnitude of the ratio $W_a/\gamma_{\ell v}$ is the ratio between the strength of a liquid-solid interatomic bond and the strength of a liquid-liquid interatomic bond. Eqn. (17) shows that no contact angle exists if $W_a > 2\gamma_{\ell v}$ (spreading situation), while we get a wetting situation $(0 < \vartheta_c < \pi/2)$ if $1 < \frac{W_a}{\gamma_{\ell v}} < 2$ and a non-wetting situation $(\frac{\pi}{2} < \vartheta_c < \pi)$ if $0 < \frac{W_a}{\gamma_{\ell v}} < 1$.

A more general case of intersection between three interfaces is as depicted in the adjoining sketch. In applying the method of interface intersections to solid surfaces (e.g. in the study of the equilibrium shapes of grooves formed where a grain



[+] Notice that the vertical component $\gamma_{\ell v} \sin\vartheta_c$ is not balanced in the above drawing. The equilibrium shape for the sessile liquid drop, to be achieved after sufficiently long times, should be lenticular, i.e. . A local distortion or "puckering" of the solid in response to the vertical component of the tension is supposed to take place near the three-phase contact line to allow a balance of vertical forces in the absence of a full equilibrium situation.

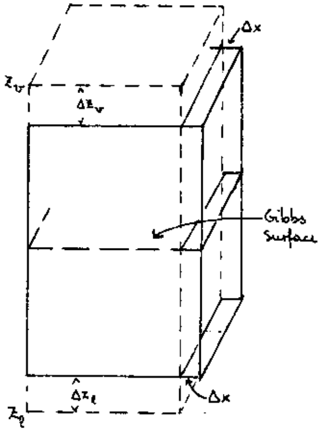
boundary intersects a solid surface), one must however keep account of the anisotropy of the surface tension, i.e. its dependence on the crystal plane. The surface tensions are acting in such a way as to change the orientation of the other interfaces, which in turn changes the surface tensions of these interfaces: this orientation effect can be described by forces acting on each boundary and tending to orientate it to a low-γ orientation. The general form of the equilibrium condition is (Herring[8])

$$\sum_{i=1}^{3}\left(\gamma_i \underset{\sim}{t}_i + \frac{\partial \gamma_i}{\partial \underset{\sim}{t}_i}\right) = 0 \,, \qquad (18)$$

where the three interfaces have surface tensions γ_i acting in directions $\underset{\sim}{t}_i$.

The method of studying the equilibrium structure of a solid surface where a grain boundary emerges has been extensively used in evaluating the relative magnitudes of grain boundary and surface free energies. Applications to solid-liquid interfacial free energies have also been made. For a discussion see e.g. the book of Woodruff[9], especially for what concerns the accuracy of presently known values of $\gamma_{s\ell}$.

Appendix 1. Relation between surface tension and tangential pressure



We consider a column of fluid with unit cross-section, on which we perform two isothermal reversible processes:

(i) we compress the liquid by Δz_ℓ and the vapour by Δz_v;

(ii) we expand the cross-section by Δx, in such a manner that the volume is unchanged, i.e. $\Delta z_\ell + \Delta z_v = (z_v - z_\ell)\,\Delta x$.

The total work is $\gamma \Delta x = \Delta w_1 + \Delta w_2$, with

$$\Delta w_1 = P(\Delta z_\ell + \Delta z_v) = P(z_v - z_\ell)\,\Delta x = P\Delta x \int_{z_\ell}^{z_v} dz$$

$$\Delta w_2 = -\int_{z_\ell}^{z_v} P_t(z)\,\Delta x\, dz\,.$$

Hence

$$\gamma = \int_{z_\ell}^{z_v} dz \left[P - P_t(z)\right].$$

The integration limits can be replaced by $\int_{-\infty}^{\infty}$, since outside the transition region the tangential pressure rapidly approaches P.

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2. Statistical mechanics of the liquid surface

Statistical mechanical theories of the liquid-vapour interface, which go back to the early work of van der Waals[10], aim at calculating the density profile $n(z)$ and the surface tension γ from an assumed interatomic force law. Two main lines of approach may be distinguished: the approach of Kirkwood and Buff[11] focusses on the surface stress tensor for the case of pairwise interatomic forces, and the approach systematized by Triezenberg and Zwanzig[12] uses general fluctuation-theory results for an inhomogeneous fluid (for a recent review see Evans[13]). We shall give a brief mention of the former approach and then focus on the fluctuation approach. The main role in the two approaches is played by the distribution function $n_2(\underset{\sim}{r},\underset{\sim}{r}')$ of pairs of atoms and by the corresponding direct correlation function $c(\underset{\sim}{r},\underset{\sim}{r}')$, respectively, and it will be useful to briefly review the main properties of these functions for a homogeneous fluid before plunging into the interface problem.

2.1 Pair distribution and direct correlation function

The pair distribution function $n_2(\underset{\sim}{r},\underset{\sim}{r}')$ is the average density of pairs of atoms such that one atom is located at $\underset{\sim}{r}$ and the second at $\underset{\sim}{r}'$. In a homogeneous fluid it depends only on $R = |\underset{\sim}{r}-\underset{\sim}{r}'|$ and is conventionally written as $n_2(R) = n^2 g(R)$. The corresponding direct correlation function $c(R)$ is defined by the Ornstein-Zernike integral equation

$$g(R) - 1 = c(R) + n\int d\underset{\sim}{R}'\, c(|\underset{\sim}{R}-\underset{\sim}{R}'|)\left[g(R')-1\right]. \qquad (1)$$

In Fourier transform we write

$$\begin{cases} g(R) = 1 + \dfrac{1}{(2\pi)^3 n}\displaystyle\int d\underset{\sim}{k}\; e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}}\left[S(k)-1\right] \\[2ex] c(R) = \dfrac{1}{(2\pi)^3 n}\displaystyle\int d\underset{\sim}{k}\; e^{-i\underset{\sim}{k}\cdot\underset{\sim}{R}}\;\hat{c}(k) \end{cases}$$

and hence eqn (1) becomes

$$1 - \hat{c}(k) = {}^{1}/_{S(k)}\,. \qquad (2)$$

$S(k)$ is the structure factor measured in a diffraction experiment (see the lectures of Prof. Enderby). The importance of $\hat{c}(k)$ in theories of liquid structure has been highlighted in the lectures of Prof. March.

For our future discussions it is important to stress the meaning of the two sides of eqn (2) in terms of the response of the fluid to an external perturbation, in the case where classical statistical mechanics applies. We first recall that $S(k$ [illegible] dynamic structure factor $S(k,\omega)$

for coherent inelastic scattering, over all energy transfers:

$$S(k) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, S(k,\omega). \tag{3}$$

We next introduce the density response function $\chi(k,\omega)$ which gives the density change $\delta n(\underset{\sim}{k},\omega)$ in Fourier transform) of the fluid in response to a weak external potential $V_{ext}(\underset{\sim}{k},\omega)$ as

$$\delta n(\underset{\sim}{k},\omega) = \chi(k,\omega)\, V_{ext}(\underset{\sim}{k},\omega)\,, \tag{4}$$

and recall that the fluctuation-dissipation theorem relates $\mathrm{Im}\,\chi(k,\omega)$ to the dissipation of energy and momentum into the fluid and hence to the inelastic scattering cross-section as

$$\mathrm{Im}\,\chi(k,\omega) = +\frac{n}{2\hbar}\left[1 - e^{-\hbar\omega/k_BT}\right] S(k,\omega) \underset{\left(\substack{\text{classical}\\ \text{limit}}\right)}{\longrightarrow} +\frac{n\omega}{2k_BT}\, S(k,\omega). \tag{5}$$

The last step is to use the Kramers-Kronig relation to evaluate the static response function $\chi(k) \equiv \chi(k,\omega=0)$:

$$\chi(k) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi}\, \frac{\mathrm{Im}\,\chi(k,\omega)}{\omega} \underset{\left(\substack{\text{classical}\\ \text{limit}}\right)}{=} +\frac{n}{k_BT}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\, S(k,\omega) = +\frac{n}{k_BT}\, S(k). \tag{6}$$

Hence $S(k)$, being simply proportional to $\chi(k)$, measures the "generalized softness" of the fluid to a density perturbation of wave number k – eqn. (6) is in fact the generalization to arbitrary wave number of the famous Ornstein-Zernike relation for a monatomic classical fluid

$$\lim_{k\to 0} S(k) = n k_BT K \tag{7}$$

where the isothermal compressibility K measures the "softness" of the fluid to a uniform squeeze. We then see from eqn. (2) that the quantity $1-\hat{c}(k)$ represents the "generalized stiffness" of the fluid.

Moving now to an inhomogeneous (monatomic) classical fluid, we define the direct correlation "function" $c(\underset{\sim}{r},\underset{\sim}{r}')$ (which is in fact a matrix in $\underset{\sim}{r}$ and $\underset{\sim}{r}'$) in such a manner that the matrix

$$K(\underset{\sim}{r},\underset{\sim}{r}') \equiv \frac{\delta(\underset{\sim}{r}-\underset{\sim}{r}')}{n(\underset{\sim}{r})} - c(\underset{\sim}{r},\underset{\sim}{r}') \tag{8}$$

is the inverse of the matrix

$$K^{-1}(\underset{\sim}{r},\underset{\sim}{r}') \equiv n_2(\underset{\sim}{r},\underset{\sim}{r}') - n(\underset{\sim}{r})\,n(\underset{\sim}{r}'). \tag{9}$$

$K^{-1}(\underset{\sim}{r},\underset{\sim}{r}')$ measures the "softness" of the inhomogeneous fluid to an external potential, and $K(\underset{\sim}{r},\underset{\sim}{r}')$ measures its "stiffness". It is this interpretation of $K(\underset{\sim}{r},\underset{\sim}{r}')$ which is basic in the fluctuation approach to the liquid-vapour interface, as it will allow us to express through this matrix the free energy change associated with fluctuations in the density profile.

2.2 Surface stress and surface tension for pairwise interatomic forces

The approach of Kirkwood and Buff[11] involves the pair distribution function $n_2(\underset{\sim}{r},\underset{\sim}{r}')$, which in the case of a planar interface is a function of the vector $\underset{\sim}{R} = \underset{\sim}{r}-\underset{\sim}{r}'$ and of the coordinate z of the first atom. An interatomic potential of the form $\varphi(R)$, depending only on the relative distance R of a pair of atoms, is assumed. The tangential pressure $P_t(z)$ can then be expressed as

$$P_t(z) = k_BT\, n(z) - \frac{1}{2}\int d\underset{\sim}{R}\, \frac{X^2}{R}\,\varphi'(R)\, n_2(\underset{\sim}{R},z) \tag{10}$$

where we write the components of $\underset{\sim}{R}$ as (X,Y,Z) and $\varphi'(R) = d\varphi(R)/dR$. Far away from the interface the z dependence disappears and eqn. (10) reduces to

$$P = k_BT n - \frac{1}{6}\int d\underset{\sim}{R}\; R\varphi'(R)\, n_2(R). \tag{11}$$

An expression similar to (10) holds for the normal pressure P_n and by imposing hydrostatic equilibrium (i.e. P_n independent of z) one finds an equation for the equilibrium density profile,

$$k_BT\,\frac{dn(z)}{dz} = \int d\underset{\sim}{R}\; \frac{Z}{R}\,\varphi'(R)\, n_2(\underset{\sim}{R},z). \tag{12}$$

Finally from eqn (1.4) one finds

$$\gamma = \frac{1}{2}\int_{-\infty}^{\infty} dz \int d\underset{\sim}{R}\; \frac{X^2-Z^2}{R}\,\varphi'(R)\, n_2(\underset{\sim}{R},z). \tag{13}$$

Needless to say, it is very difficult to calculate $n_2(\underset{\sim}{R},z)$ and therefore all the work based on this method has had to relate n_2 to the bulk pair function and to $n(z)$. The most drastic simplification is to take the liquid as homogeneous up to the Gibbs surface and to assume that the vapour has negligible density, whereby one recovers from (13) an expression for γ due to Fowler[14],

$$\gamma \approx \frac{\pi}{8}\, n_\ell^2 \int_0^{\infty} dR\; \varphi'(R)\, R^4\, g(R). \tag{14}$$

A delicate point in these calculations is the consistency between $\varphi(R)$ and $g(R)$, because of the strong sensitivity to the relative positions of the maximum in $\varphi'(R)$ and the first maximum in $g(R)$. Using computer simulation data as input, McDonald and Freeman[15] find for liquid neon reasonable results with (14) and an improvement of the results when they allow a smooth density profile of finite thickness. For a more detailed discussion of this approach the article of Berry[16] may be consulted.

2.3 Density profile equation for inhomogeneous fluid and fluctuation approach to surface tension

The Helmholtz free energy F of an inhomogeneous fluid can be written in terms of a position-dependent free energy density $f(\mathbf{r})$ as

$$F = \int d\mathbf{r}\; f(\mathbf{r}) \,. \tag{15}$$

The basis of the theory is the theorem of Hohenberg, Kohn and Mermin[17], which shows that $f(\mathbf{r})$ is a unique functional of the density profile $n(\mathbf{r}')$: namely, $f(\mathbf{r})$ is uniquely determined (in principle, of course!) if the density $n(\mathbf{r}')$ is known at all points $\mathbf{r}'$ in the system.

Let us consider the fluid under an external potential $V_{ext}(\mathbf{r})$ which determines a density profile $n(\mathbf{r})$, and define

$$u(\mathbf{r}) \equiv \beta\left[\mu - V_{ext}(\mathbf{r})\right] \qquad \left(\beta = 1/k_BT \,,\ \mu = \text{chemical potential}\right). \tag{16}$$

The HKM theorem ensures that there is a unique functional relationship between $u(\mathbf{r})$ and $n(\mathbf{r}')$, symbolically written as

$$u(\mathbf{r}) = u(\mathbf{r};[n(\mathbf{r}')]) \,. \tag{17}$$

Considering now a rigid translation of the whole system by an amount $\boldsymbol{\delta}$, we have

$$u(\mathbf{r}+\boldsymbol{\delta}) = u(\mathbf{r};[n(\mathbf{r}'+\boldsymbol{\delta})]) \tag{18}$$

(visualize this equation by a drawing!). In the limit $\boldsymbol{\delta}\to 0$ this yields by Taylor expansion

$$\nabla u(\mathbf{r}) = \int d\mathbf{r}'\; K(\mathbf{r},\mathbf{r}')\,\nabla n(\mathbf{r}') \tag{19}$$

where

$$K(\mathbf{r},\mathbf{r}') \equiv \delta u(\mathbf{r})/\delta n(\mathbf{r}') \tag{20}$$

(the symbol $\delta u(\mathbf{r})/\delta n(\mathbf{r}')$ denotes the functional derivative of $u(\mathbf{r})$ with respect to $n(\mathbf{r}')$, i.e. the change in the value of u at $\mathbf{r}$ due to a change in n at $\mathbf{r}'$). From the definition (20) it is clear that $K(\mathbf{r},\mathbf{r}')$ has the meaning of an inverse density response matrix, and in fact it coincides with the definition (8) for a classical fluid. Using that expression in eqn (19) and taking the limit $u\to 0$, we find

$$\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})} = \int d\mathbf{r}'\; c(\mathbf{r},\mathbf{r}')\,\nabla n(\mathbf{r}') \tag{21}$$

as the equation which determines the equilibrium density profile in an inhomogeneous fluid.

For the case of a planar liquid-vapour interface the matrix $c(\mathbf{r},\mathbf{r}')$ depends only on z, z' and $s = \left[(x-x')^2+(y-y')^2\right]^{1/2}$. Taking the two-dimensional Fourier transform

$$\hat{c}(k;z,z') = \int d^2\mathbf{s}\; e^{i\mathbf{k}\cdot\mathbf{s}}\; c(s;z,z') \tag{22}$$

we therefore find

$$\frac{dn(z)}{dz} = n(z)\int_{-\infty}^{\infty} dz'\; c_0(z,z')\,\frac{dn(z')}{dz'} \tag{23}$$

where $c_0(z,z') \equiv \hat{c}(k=0;z,z') = \int d^2s\; c(s;z,z')$. This equation (which should be contrasted with eqn (12) for the Kirkwood-Buff approach) is the equilibrium condition in the fluctuation approach of Triezenberg and Zwanzig[12]. Their derivation involves examining the effect of a long-wavelength fluctuation of the Gibbs surface, with wave vector along the surface: to lowest order in the wave number of the fluctuation, this corresponds to a rigid translation of the system and eqn (23) follows from the fact that neither a free energy change nor a surface area change accompanies such a translation.

Such changes arise at the next order in the wave number of the fluctuation and their evaluation leads to an expression for the surface tension. In particular the free energy change for a small fluctuation $\Delta n(\mathbf{r})$ in the density profile can be written

$$\Delta F = \tfrac{1}{2}k_BT \iint d\mathbf{r}\, d\mathbf{r}'\; \Delta n(\mathbf{r})\, K(\mathbf{r},\mathbf{r}')\, \Delta n(\mathbf{r}') \,, \tag{24}$$

this being an obvious generalization of the usual elasticity-theory expression through the use of the "stiffness" matrix $K(\mathbf{r},\mathbf{r}')$. A detailed calculation, for which we refer to the original paper[12], yields

$$\gamma = k_BT \iint_{-\infty}^{\infty} dz\, dz'\; \frac{dn(z)}{dz}\, c_2(z,z')\, \frac{dn(z')}{dz'} \tag{25}$$

where $c_2(z,z') \equiv \frac{1}{4}\int d^2\mathbf{s}\; s^2 c(s;z,z') = -\frac{1}{4}\left(d^2\hat{c}(k;z,z')/dk^2\right)_{k\to 0}$.

Eqns (23) and (24) are formally exact and independent of the detailed nature of the interatomic forces. Of course the functions c_0 and c_2 for the inhomogeneous fluid are not known. The theory becomes practicable when these are related to properties of the homogeneous fluid, as one does in practice through the "square density gradient" approximation that we proceed to discuss below.

2.4 Density-gradient expansion and square-gradient approximation

We now return to eqn (15) and let us be guided by the Cahn-Hilliard argument (§1.2) in the search for a useful but approximate expression for the free energy density $f(z)$ as a functional of the density profile $n(z)$ for the planar interface. In the case where $n(z)$ were slowly varying with z, it would be reasonable to represent $f(z)$ by a local term $f(n(z))$ (the free energy density of a homogeneous fluid at the local atomic density $n(z)$) plus an infinite series involving derivatives of $n(z)$ and their powers. The Cahn-Hilliard argument suggests that it may be already useful to include only the leading correction in $n'(z) \equiv dn(z)/dz$, which by symmetry is the square power $[n'(z)]^2$. We thus write

$$f(z) \simeq f(n(z)) + \tfrac{1}{2} a(n(z)) [n'(z)]^2 \qquad (26)$$

The function $a(n(z))$ is again a property of the homogeneous fluid, and one can show[17,18] that

$$a = \tfrac{1}{6} k_B T \int d\underset{\sim}{r}\, r^2 c(r), \qquad (27)$$

$c(r)$ being the direct correlation function of the homogeneous fluid at density $n(z)$. Notice that, since $n(z)$ changes continuously from n_ℓ to n_v across the interface, eqn (26) requires that we know f and a for the homogeneous fluid also in the density region where it is unstable relative to two-phase separation.

Let us examine[18] in some detail the consequences of eqn (26). The equilibrium condition can be found by minimizing F at constant N, i.e. by minimizing the integral $\int_{-\infty}^{\infty} dz\, [f(z) - \mu n(z)]$: the "Lagrange multiplier" μ is the chemical potential and hence $\omega(z) \equiv \mu n(z) - f(z)$ is the density of "thermodynamic potential" Ω ($\Omega = -PV = \mu N - F$ in standard thermodynamics). The Euler-Lagrange equation for such a variational problem, involving both $n(z)$ and $n'(z)$, is

$$\frac{\partial \omega(z)}{\partial n(z)} - \frac{d}{dz} \frac{\partial \omega(z)}{\partial n'(z)} = 0$$

and hence

$$\mu = \mu(n(z)) - a(n(z))\, n''(z) - \tfrac{1}{2} a'(n(z)) [n'(z)]^2, \qquad (28)$$

where $\mu(n(z)) \equiv \dfrac{\partial f(n(z))}{\partial n(z)}$ and $a' = \dfrac{\partial a(n)}{\partial n}$. This equilibrium condition determines the density profile $n(z)$.

By multiplying eqn (28) by $n'(z)$, we can rewrite it as

$$\frac{d}{dz} \left\{ \mu n(z) - f(n(z)) + \tfrac{1}{2} a(n(z)) [n'(z)]^2 \right\} = 0 \qquad (28')$$

and hence by integration we get

$$\mu n(z) - f(n(z)) + \tfrac{1}{2} a(n(z)) [n'(z)]^2 = P \qquad (29)$$

where we have identified the constant of integration with the pressure P by taking the limit $z \to \pm\infty$ of the left-hand side ($P = \mu n_\ell - f(n_\ell) = \mu n_v - f(n_v)$). Equation (29) expresses the condition of mechanical equilibrium of the interface, and we show in Appendix 2 that it is equivalent[18] to the well-known Maxwell construction.

Finally, we can relate the surface tension to the density profile by using eqn (1.3) and noticing that $V_\ell f(n_\ell) + V_v f(n_v) = \mu N - PV$:

$$\begin{aligned} \gamma &= \int_{-\infty}^{\infty} dz \left\{ f(n(z)) + \tfrac{1}{2} a(n(z)) [n'(z)]^2 - \mu n(z) + P \right\} \\ &= \int_{-\infty}^{\infty} dz\, a(n(z)) [n'(z)]^2, \end{aligned} \qquad (30)$$

where we have used eqn (29). To see the connection[19] with the Cahn-Hilliard argument, we expand $f(n(z))$ around the liquid density n_ℓ.

$$f(n(z)) = f(n_\ell) + [n(z) - n_\ell] \left.\frac{\partial f}{\partial n}\right|_{n=n_\ell} + \tfrac{1}{2} [n(z) - n_\ell]^2 \left.\frac{\partial^2 f}{\partial n^2}\right|_{n=n_\ell} + \cdots$$

and use $\left.\frac{\partial f}{\partial n}\right|_{n_\ell} = \mu(n_\ell) = \mu$, $n_\ell^2 \left.\frac{\partial^2 f}{\partial n^2}\right|_{n_\ell} = 1/K$. Using again eqn (29) to eliminate a, we find

$$\gamma = 2 \int_{-\infty}^{\infty} dz\, [f(n(z)) - \mu n(z) + P] \simeq \frac{1}{K} \int_{-\infty}^{\infty} dz \left(\frac{n(z) - n_\ell}{n_\ell} \right)^2 \qquad (31)$$

displaying again the relation between the product γK and the interfacial thickness.

This simple treatment can easily be extended[18] to the case where the fluid is in an external potential $U(z)$ - e.g. a gravitational potential. Eqn (26) must be supplemented by a term $n(z) U(z)$ and the equilibrium condition becomes

$$\frac{dP(z)}{dz} = -n(z) \frac{dU}{dz}, \quad P(z) = \mu n(z) - f(n(z)) - n(z) U(z) + \tfrac{1}{2} a(n(z)) [n'(z)]^2, \qquad (32)$$

this being the differential form of Bernoulli's theorem in the absence of flow. Non-planar interfaces can also be treated - for instance the case[18] of a spherical liquid drop inside its vapour, for which one recovers the Young-Laplace formula. A number of numerical applications to specific systems can be found in the recent literature. For extensions to multicomponent systems and to fluids of charged particles, see ref. 20.

2.5 Liquid metals.

A simple theory[illegible] for the surface tension of a liquid metal can be built by focussing attention on the behaviour of the conduction electrons. At the most elementary level one constructs[21] the analogue of eqn (26) as the sum of a local energy term $\varepsilon(n)$ (the kinetic, exchange and correlation energy of a homogeneous electron gas at density n) and of an inhomogeneity term in $(\underset{\sim}{\nabla} n)^2$ associated with kinetic effects. To estimate the latter, we can use a simplified argument: the kinetic energy of an electron is

$$KE = -\frac{\hbar^2}{2m} \int d\underset{\sim}{r}\, \psi \nabla^2 \psi = \frac{\hbar^2}{2m} \int d\underset{\sim}{r}\, (\underset{\sim}{\nabla} \psi)^2 = \frac{\hbar^2}{8m} \int d\underset{\sim}{r}\, (\underset{\sim}{\nabla} n)^2 / n$$

since for a single electron $\psi = n^{1/2}$. We thus write the analogue of eqns (15) and (26) as

$$E = \int d\underset{\sim}{r} \left[\varepsilon(n) + \frac{\lambda \hbar^2}{8m} \frac{(\underset{\sim}{\nabla} n)^2}{n} \right] \qquad (33)$$

where λ is a numerical factor (the theory of the inhomogeneous Fermi gas yields[22] $\lambda = 1/9$). The variational principle $\delta(E - \mu n)/\delta n = 0$ yields (the calculation is fully analogous to the derivation of eqn (28))

$$-\frac{\lambda \hbar^2}{4m} \left[\frac{n''}{n} - \frac{1}{2} \left(\frac{n'}{n} \right)^2 \right] + \frac{d\varepsilon}{dn} = \mu \qquad (34)$$

for the determination of the equilibrium density $n(z)$. Setting $n = \psi^2$, this is formally equivalent to a Schroedinger equation of the form

$$-\frac{\lambda \hbar^2}{2m} \frac{d^2 \psi}{dz^2} + \left(\frac{d\varepsilon}{dn} - \mu \right) \psi = 0. \qquad (35)$$

The surface tension, defined as the energy difference between the inhomogeneous electron gas and a homogeneous electron gas, per unit surface area, is given in analogy with eqn (30) by

$$\gamma = \frac{\lambda \hbar^2}{m} \int_{-\infty}^{\infty} dz\, [\psi'(z)]^2. \qquad (36)$$

This elementary theory has the advantage that it can be carried through analytically for certain simple forms of $\mathcal{E}(n)$ – in particular for the case

$$\mathcal{E}(n) = b\,n\left[\left(\frac{n}{n_0}\right)^{2/3} - 2\left(\frac{n}{n_0}\right)^{1/3}\right] \qquad (37)$$

which corresponds to the sum of a kinetic energy term ($\propto n^{5/3}$) and an exchange energy term ($\propto n^{4/3}$). Clearly n_0 is the equilibrium density at zero pressure $\left(P = \frac{d[\mathcal{E}(n)/n]}{dn}\Big|_{n_0}\right)$ and b is $-\mu$ $\left(\mu = \frac{d\mathcal{E}(n)}{dn}\Big|_{n_0}\right)$; the corresponding electron-gas compressibility is $K^{-1} = \left(n^2 \frac{d^2\mathcal{E}(n)}{dn^2}\right)_{n_0} = \frac{2}{9} n_0 b$. The solution of (34) is

$$n(z)/n_0 = \left[1 + B\exp(z/l)\right]^{-3}$$

where B is a constant and the length l, which clearly measures the surface thickness, is given by

$$l = \left(9\lambda\hbar^2/8mb\right)^{1/2}. \qquad (38)$$

From (36) one finally finds

$$\gamma = \frac{1}{4} n_0 \left(\frac{b\lambda\hbar^2}{2m}\right)^{1/2} \quad \text{or} \quad \gamma K = \frac{3}{4} l. \qquad (39)$$

An important advance of more refined theories of the electronic surface density profile[23] is to avoid a density gradient expansion for the electronic kinetic energy. The equilibrium condition for the profile is still formulated as a Schroedinger equation, in which however the Laplacian term accounts for the full single-electron kinetic energy and the potential term includes exchange and correlation terms. A Hartree-like term for the electron-ion interaction also arises if the ionic and electronic density profiles differ from each other (in the above discussion we have tacitly assumed that they coincide - this approximation should be better for liquid metals than for crystalline metals). For a review of work mostly directed to solid surfaces see also the article of Appelbaum and Hamann.[24] No detailed consideration has as yet been given to the transition from metallic to molecular binding in the transition region from liquid to vapour.

2.6 Surface tension and cleavage work

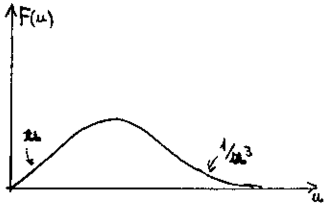
In the spirit of the foregoing discussion, which has stressed the usefulness of approximately relating surface properties to bulk properties, we wish to discuss at this point a simple approach recently developed for solid metals at $T=0$ by Kohn and Yaniv,[25] subsequently extended to electron-hole liquids in semiconductors.[26] The surface tension is viewed as the reversible work needed to separate two half-crystals to infinite distance from each other and expressed as

$$\gamma = \frac{1}{2}\int_0^\infty du\, F(u) \qquad (40)$$

where $F(u)$ is the force per unit area needed to displace by u the two half-crystals. Using elasticity theory for small displacements and the Lifshitz theory of van der Waals interactions at large displacements, one has

$$F(u) = \begin{cases} Au & \text{for } u \ll a \\ C/u^3 & \text{for } u \gg a \end{cases} \qquad (41)$$

where a is the near-neighbour distance, A is a suitable elastic constant and C is a van der Waals constant. The qualitative shape of $F(u)$ is indicated in the sketch.



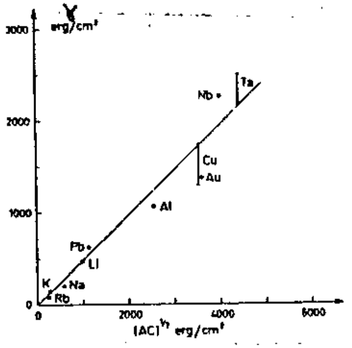
To interpolate between the above known limits, Kohn and Yaniv introduce a hypothesis of universality, $F(u) = B f(u/u_0)$ where $f(\xi)$ is a universal function (at least for similar materials) of a scaled displacement $\xi = u/u_0$. Contact with the limits (41) yields

$$F(u) = \left(A^3C\right)^{1/4} f\left(u/u_0\right) \quad \text{with} \quad u_0 = \left(C/A\right)^{1/4} \qquad (42)$$

and

$$\gamma = \alpha\,(AC)^{1/2} \qquad (43)$$

where $\alpha \equiv \frac{1}{2}\int_0^\infty d\xi\, f(\xi)$ should be a universal constant, at least for similar materials. The test of eqn (43) for solid metals is reported in the adjoining figure.



The empirical value of α is $\alpha = 0.476$ for metals, which is very close to the value $\alpha = 1/2$ that one would obtain by using

$$f(\xi) = \begin{cases} \xi & \text{for } \xi \le 1 \\ \xi^{-3} & \text{for } \xi \ge 1 \end{cases}$$

Adopting this form we can also write

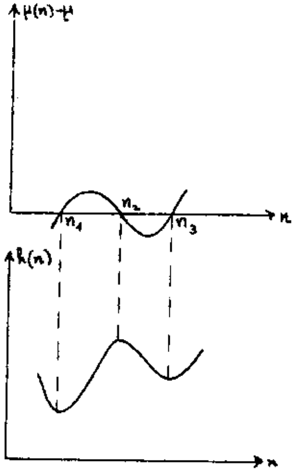
$$\gamma \simeq \frac{1}{2} A u_0^2$$

and for a liquid, taking $A \simeq (aK)^{-1}$, we get

$$\gamma K \simeq \frac{u_0^2}{2a}.$$

It is of course not surprising that a relation should exist between the surface thickness and the displacement u_0 at which the cleavage force $F(u)$ has its maximum.

Appendix 2. Equivalence between eqn. (29) and the Maxwell construction



The integral of eqn (28) can be rewritten as

$$\frac{1}{2}\, a(n(z))\,[n'(z)]^2 = \int_{\bar{n}}^{n(z)} dn\,[\mu(n)-\mu] + C \equiv h(n)$$

where C is a constant of integration and the lower limit $\bar{n}$ of the integral is unspecified. According to (28), this equation must be solved for the two-phase system with the condition $\mu(n)-\mu \to 0$ for $z \to +\infty$ ($n \to n_{s}$) and $z \to -\infty$ ($n \to n_{\ell}$), where $n'(z)=0$.

The function $\mu(n)$ is expected to have a typical van der Waals shape, and we assume that $\mu(n)-\mu$ has three zeroes (in the case of only one or two zeroes, only a homogeneous system is a possible solution). The function $h(n)$ correspondingly has two minima and a maximum. With different choices of the constant C we can force $h(n)$ to vanish either at n_1 or at n_3 (the solution $n=n_2$ is unstable because the corresponding compressibility is negative). Only if the two minima in $h(n)$ have the same value can we make $h(n)$ vanish simultaneously at n_1 and n_3, thus finding the physical solution for the two-phase system. The condition for this to happen is

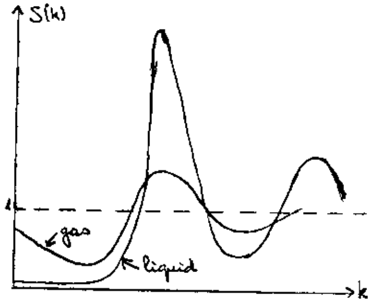
$$\int_{n_1}^{n_2} [\mu(n)-\mu]\, dn + \int_{n_2}^{n_3} [\mu(n)-\mu]\, dn = 0 .$$

At a given temperature there is only one value of μ (the chemical potential at coexistence of the two phases) which allows us to satisfy this condition.

3. Liquid-solid transition and the structure of the liquid-solid interface

Our current microscopic understanding of the liquid-solid interface is still rather primitive[9,27,28]. We consider here first of all the equilibrium between the liquid and the solid phase at the freezing point, by describing a recent theory of freezing[29] in a monatomic system (as a solid-liquid equilibrium problem rather than as a homogeneous nucleation problem, as in §1.4) and its extension[30] to ionic liquids. We next briefly review recent developments in the theory of melting[31], which stress the role of lattice defects in this process. The rest of the discussion is given to the structure of the liquid-solid interface and its relevance to crystal growth.

3.1 Theory of freezing



Bearing in mind the meaning of the structure factor S(k) as a "generalized softness function" for a monatomic liquid (see §2.1), we look in the adjoining sketch at this object for two different thermodynamic states, (i) a real gas and (ii) a liquid near freezing. It is qualitatively clear from the shape of this function that not only is the liquid much harder to compress (see eqn.(2.7)), but also it is considerably "softer" against a density-wave deformation with wave number lying in the region of the main peak of S(k) – and also in the region of the subsequent peak.

Hansen and Verlet[32] have emphasised an empirical relation between the height of the main peak in S(k) for a monatomic liquid and its freezing. An illustration for the alkali metals is reported in the adjoining table: this reports also the case of the one-component classical plasma on a uniform neutralizing background (OCP), which can be regarded as a prototype model for these metals[33]. Rough equivalent criteria for freezing can clearly be formulated from these data: freezing occurs in these systems

	Li	Na	K	Rb	Cs	OCP
$\Gamma_f = \dfrac{e^2}{a k_B T_f}$:	211	208	186	188	181	177
S_{peak} at T_f :	–	2.8÷3.1	2.7÷3.1	~3.	~3.	~3.
$\exp(-2W_{G_1})$:	0.64	0.66	0.65	0.67	0.63	0.62

when the "plasma peramater" $\Gamma \equiv e^2/ak_BT$ (which measures the ratio of the ionic potential energy to the thermal energy) reaches[34] a value of $\approx 180 \div 200$, or alternatively when the main peak in $S(k)$ reaches[32] a value of ≈ 3. The last row of the table shows that the latter freesing criterion is not unrelated to the well known Lindemann criterion for melting: it reports the Debye-Waller factor of the solid phase at melting, calculated at the first reciprocal lattice vector $\underset{\sim}{G}_1$, and this quantity clearly measures the ratio of the mean square displacement to the lattice constant.

These considerations lie behind the theory of freesing of Ramakrishnan and Yussouff[29]. In a simplified derivation of the theory[35], we start from eqn (2.21) for the equilibrium density profile of an inhomogeneous system,

$$\underset{\sim}{\nabla} n(\underset{\sim}{r})/n(\underset{\sim}{r}) = \int d\underset{\sim}{r}'\ c(\underset{\sim}{r},\underset{\sim}{r}')\,\underset{\sim}{\nabla} n(\underset{\sim}{r}') \qquad (1)$$

and, after noticing that it is trivially satisfied by the homogeneous liquid phase (where $c(\underset{\sim}{r},\underset{\sim}{r}')=c_\ell(|\underset{\sim}{r}-\underset{\sim}{r}'|)$ and $n(\underset{\sim}{r})=n_\ell$), we ask whether it will admit at some point a second solution in equilibrium with the homogeneous-liquid solution. We require that this second solution should have the form of a periodic density,

$$n_p(\underset{\sim}{r}) = n_s + \frac{1}{V}\sum_{\underset{\sim}{G}\neq 0} n_{\underset{\sim}{G}}\, e^{i\underset{\sim}{G}\cdot\underset{\sim}{r}} \qquad (\underset{\sim}{G} = \text{reciprocal lattice vectors}) \qquad (2)$$

and that it should arise as a bifurcation of the solution of the equilibrium equation as we approach the coexistence point from the homogeneous-liquid phase – i.e. that it should satisfy eqn (1) with $c(\underset{\sim}{r},\underset{\sim}{r}')$ replaced by $c_\ell(|\underset{\sim}{r}-\underset{\sim}{r}'|)$. We shall next have to impose also that the free energies of the two solutions are equal at coexistence.

From eqn (1), rewritten as

$$\underset{\sim}{\nabla} n(\underset{\sim}{r})/n(\underset{\sim}{r}) = \int d\underset{\sim}{r}'\ c_\ell(|\underset{\sim}{r}-\underset{\sim}{r}'|)\,\underset{\sim}{\nabla} n(\underset{\sim}{r}') \qquad (n(\underset{\sim}{r}) = n_p(\underset{\sim}{r}) \text{ or } n_\ell) \qquad (3)$$

upon integration of the right-hand side by parts we have

$$\underset{\sim}{\nabla} n(\underset{\sim}{r})/n(\underset{\sim}{r}) = \int d\underset{\sim}{r}'\ \underset{\sim}{\nabla}_{r}\, c_\ell(|\underset{\sim}{r}-\underset{\sim}{r}'|)\, n(\underset{\sim}{r}') \qquad (3')$$

and this can next be integrated over $\underset{\sim}{r}$ to obtain at the coexistence point

$$\ln\left(\frac{n_p(\underset{\sim}{r})}{n_\ell}\right) = \int d\underset{\sim}{r}'\ c_\ell(|\underset{\sim}{r}-\underset{\sim}{r}'|)\,\left[n_p(\underset{\sim}{r}') - n_\ell\right]. \qquad (4)$$

Our next step is to construct the difference $\Delta\Omega$ in thermodynamic potential between the two phases in such a manner that eqn (4) follows from it as the Euler equation of a minimum-free-energy principle:

$$\frac{\Delta\Omega}{k_BT} = \int d\underset{\sim}{r}\left[n_p(\underset{\sim}{r})\ln\left(\frac{n_p(\underset{\sim}{r})}{n_\ell}\right) - \{n_p(\underset{\sim}{r}) - n_\ell\}\right] - \frac{1}{2}\iint d\underset{\sim}{r}\,d\underset{\sim}{r}'\left[n_p(\underset{\sim}{r})-n_\ell\right] c_\ell(|\underset{\sim}{r}-\underset{\sim}{r}'|)\left[n_p(\underset{\sim}{r}')-n_\ell\right]. \qquad (5)$$

The first term represent a free-particle contribution and the second is in essence available in eqn (2.24) for the Triezenberg-Zwansing theory; it is easily checked that eqn (4) follows by minimizing this expression with respect to $n_p(\underset{\sim}{r})$. Using (4) in (5) we get at the coexistence point, to within non-linear terms in $n_s - n_\ell$,

$$\Delta\Omega/k_BT = \frac{1}{2N}\sum_{\underset{\sim}{G}\neq 0}\hat{c}(\underset{\sim}{G})\,|n_{\underset{\sim}{G}}|^2 - \frac{1}{2}N\left[1-\hat{c}(k=0)\right](n_s^2 - n_\ell^2)/n_\ell^2 \qquad (6)$$

and this must be zero at coexistence. Notice that $\hat{c}(\underset{\sim}{G}) = 1 - 1/S(G)$ (eqn (2.2)) and $1-\hat{c}(0)$ is in essence the inverse compressibility of the liquid (eqns (2.2) and (2.7)).

Eqns (4) and (6) must be solved self-consistently to find the periodic density profile $n_p(\underset{\sim}{r})$ in equilibrium with the homogeneous liquid at density n_ℓ. That a solution with $\Delta\Omega = 0$ exists, is clear from the signs of the two terms in eqn (6): free energy must be expended in modulating the liquid density at wavevectors $\underset{\sim}{k} = \underset{\sim}{G} \neq 0$, but free energy can be gained from the density change term if $n_s > n_\ell$. Freesing occurs in this theory as a first-order phase transition in which the $\underset{\sim}{G}\neq 0$ components and the $\underset{\sim}{k}=0$ component of the density are strongly coupled by the non-linear nature of eqn. (4)[†].

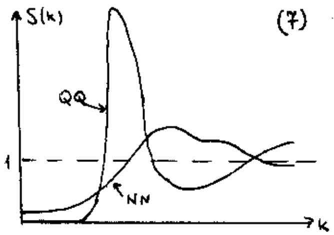
Numerical results for the freesing of sodium are reported in the adjoining table (for more complete illustrations and discussion the original work[29] should be consulted). Freesing is already obtained by allowing $n_{\underset{\sim}{G}} \neq 0$ only for $\underset{\sim}{G} = \underset{\sim}{G}_1$ (the first star of reciprocal lattice vectors) but this requires an excessive value of $S(G_1)$ (i.e. of the main peak in $S(k)$). The inclusion of the first two stars of reciprocal lattice vectors seems to work nicely, as reported in the table.

	$\hat{c}(\underset{\sim}{G}_1)$	$\hat{c}(\underset{\sim}{G}_2)$	$\Delta n/n$
Theory	0.65	0.16	0,045
Expt.	0.65	0,16	0,026

3.2 Freesing of ionic liquids

The measurement of partial structure factor $S_{\alpha\beta}(k)$ for ionic liquids by the isotope-substitution technique in neutron diffraction has been described in the lectures of Prof. Enderby. A particularly illuminating way of looking at these data is to build suitable linear combinations of the partial structure factors[36], in particular for a molten alkali halide the quantities

$$\begin{cases} S_{NN}(k) = \frac{1}{2}\left[S_{++}(k) + S_{--}(k) + 2S_{+-}(k)\right] \\ S_{QQ}(k) = \frac{1}{2}\left[S_{++}(k) + S_{--}(k) - 2S_{+-}(k)\right] \end{cases} \qquad (7)$$



By construction these describe, respectively, the autocorrelations of the total density fluctuations $n_+(k)+n_-(k)$ and the autocorrelations of the charge density fluctuations $n_+(k)-n_-(k)$. From this viewpoint a molten salt such as RbCl can be viewed[37] as a hardly compresible

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[†] Notice that, if eqn (4) is linearized by setting $\ln(n_p(\underset{\sim}{r})/n_\ell) \simeq [n_p(\underset{\sim}{r}) - n_\ell]/n_\ell$, we get $n_{\underset{\sim}{G}} \neq 0$ only if $1-\hat{c}(\underset{\sim}{G}) = 0$ i.e. only if $S(G) = \infty$: in such a case the liquid-solid transition would occur only as an instability of the liquid phase – contrary to reality!

liquid with a strong amount of short-range ordering in the ionic charge distribution (see sketch). From our preceding discussion it is clear[30] that at the simplest level a theory of freezing for such a system should focus on the coupling between the density change at the transition (whose softness parameter is $S_{NN}(k=0)$) and the modulation in the charge density $n_+(\mathbf{G}_1)-n_-(\mathbf{G}_1)$ at the first star of reciprocal lattice vectors (whose softness parameter is $S_{QQ}(G_1)$). Notice that it is the charge density that has the correct Bravais-lattice symmetry after solidification.

The adjoining table indicates in this light empirical freezing criteria for the alkali chlorides[38,39]:

	NaCl	KCl	RbCl	CsCl
$\Gamma_f = e^2/ak_BT_f$:	71	65	66	65
S_{QQ}^{peak} at :	3.2	4.4	3.6	3.1
$(T-T_f)/T_f$:	0.070	0.023	0.035	0.059

leading to $\Gamma_{\text{freezing}} \simeq 70$ and to $S_{QQ}^{\text{peak}} \sim 4 \div 5$ at freezing. The next table reports preliminary results[40] of the extension of the RY theory to RbCl, where only the first star of reciprocal lattice vectors has so far been considered.

	$\hat{c}_{QQ}(\mathbf{G}_1)$	$\hat{c}_{NN}(\mathbf{k}_2)$	$\Delta n/n$
Theory	0.93	—	0.1
Expt.	0.72	0.4	0.14

Finally we wish to mention the case of molten $BaCl_2$, in contrast to the foregoing discussion for molten alkali halides. The measured partial structure factors of this liquid system show a much stronger ordering in $S_{BaBa}(k)$ than in the other partial structure factors, and an application of the RY theory yields[30] $n_{Cl^-}(\mathbf{G}_1) \approx 0.4\, n_{Ba^{2+}}(\mathbf{G}_1)$. Namely, the chlorine component in the solid at equilibrium with the liquid can be viewed as a "liquid" modulated by the Ba^{2+} lattice rather than as an ordered Cl^- lattice. This observation is interesting because $BaCl_2$ in the high-temperature solid phase is known to be a fast anionic conductor.

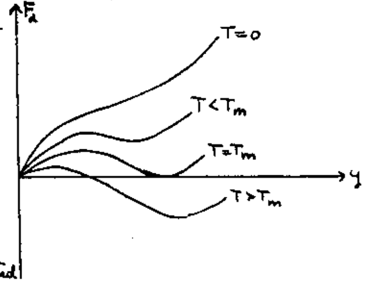
3.3 Dislocation theory of melting

An important feature of the RY theory of freezing of a simple liquid is, as we stressed in its presentation, that it accounts correctly for the first-order character of the liquid-solid transition: the $\mathbf{G} \neq 0$ Fourier components of the particle density appear suddenly with a finite value at T_m (contrary to the case of a second-order transition, where the "order parameter" increases continuously from zero at the critical temperature). Many authors in the past have tried to devise a theory of melting by viewing the liquid as a crystal which, in thermal equilibrium, contains a high concentration of some particular type of crystal defect (vacancies, dislocations, grain boundaries: for a good discussion see e.g. the book of Nabarro[41]). Recent work by Edwards and Warner[31] successfully predicts a first-order melting transition on the basis of a dislocation model in which the crucial effect arises from mutual "screening" in a dense assembly of dislocations.

Qualitatively, the main contribution to the free energy of a dislocation arises from the long-range elastic distortions induced in the material, but when dislocations of opposite Burgers vectors are brought together most of this distortion is eliminated – in fact a dense assembly of dislocations can arrange itself so as to maximize this reduction. Edwards and Warren find that the free energy of the dislocation assembly can be schematically written as

$$F_d = \rho F_1 + \rho^2 F_2 - \rho^{3/2} F_{3/2} \qquad (8)$$

where ρ is the length of dislocation lines per unit volume and the F_i's are temperature-dependent coefficients. The successive terms in this expression are in essence (i) the core energy and the entropy of the dislocations, (ii) the energy associated with the dilation induced by the dislocations, and (iii) negative term arising from many-dislocation effects. This latter term is evaluated by writing the energy of interaction of two dislocations lines as $E_{12} \propto \iint (\mathbf{b}_1 \cdot d\mathbf{l}_1)(\mathbf{b}_2 \cdot d\mathbf{l}_2)/r_{12}$, where $\mathbf{b}_i$ are the Burgers vectors, and by calculating the corresponding contribution to the partition function with techniques taken from the theory of networks of random walks. The calculated free energy, as a function of a variable $y \propto \rho/T$, has the form indicated in the adjoining sketch for various values of T.



The melting temperature T_m is identified with the temperature at which the equilibrium condition $\partial F_d/\partial y = 0$ yields a finite concentration of dislocations with no excess free energy over the undislocated crystal ($F_d=0$). The first-order character of the predicted transition is apparent from the fact that such a finite concentration of dislocations at equilibrium arises suddenly in the theory: over a finite range of temperature below T_m, one still has a local minimum of F_2 at finite y, but corresponding to a metastable situation ($F_2>0$) which may be used to describe a supercooled liquid or a glass. The original work[31] should be consulted for further details.

3.4 Molecular theory of the solid-liquid interface – a trace

Haymet and Oxtoby[42] have recently shown how the RY theory of freezing may be extended to develop a molecular theory of the solid-liquid interface. For a monatomic system as discussed by these authors, the interface region is taken to have a density profile which has again the form of eqn (2), but now the density difference n_s-n_ℓ as well as the various Fourier components $n_{\mathbf{G}}$ become functions of position across the interface. More precisely Haymet and Oxtoby write

$$n(\mathbf{r}) = n_\ell\left[1+\eta(\mathbf{r})\right] + n_\ell \sum_{\mathbf{G}\neq 0} \mu_{\mathbf{G}}(\mathbf{r})\, e^{i\mathbf{G}\cdot\mathbf{r}} \qquad (9)$$

in the interface region, with limiting values for $\eta(\mathbf{r})$ and $\mu_{\mathbf{G}}(\mathbf{r})$ which are obviously given by

$$\begin{cases} \eta(\mathbf{r}) \to (n_s-n_\ell)/n_\ell \quad \text{and} \quad \mu_{\mathbf{G}}(\mathbf{r}) \to n_{\mathbf{G}}/n_\ell V \quad \text{in the solid} \\ \eta(\mathbf{r}) \to 0 \quad \text{and} \quad \mu_{\mathbf{G}}(\mathbf{r}) \to 0 \quad \text{in the liquid} \end{cases} \qquad (10)$$

If $\eta(\mathbf{r})$ and $\mu_{\mathbf{G}}(\mathbf{r})$ are assumed to be slowly varying functions of position, so that only their square gradients need to be included, one can develop an approximate theory for the liquid-solid interface which is the analogue of the theory for the liquid-vapour interface described in § 2.4.

In the particular case of a planar liquid-solid interface, the excess thermodynamic potential per unit area can be written in this square-gradient approximation as

$$\frac{\Delta\Omega}{k_BT} = \frac{\Delta\Omega_u}{k_BT} + \frac{1}{4}\hat{c}''(k=0)\int_{-\infty}^{\infty} dz \left[\frac{d\eta(z)}{dz}\right]^2 + \frac{1}{4}\sum_{\mathbf{G}\neq 0}\hat{c}''(\mathbf{G})\, G_z^2 \int_{-\infty}^{\infty} dz \left[\frac{d\mu_{\mathbf{G}}(z)}{dz}\right]^2. \qquad (11)$$

This is supplemented by suitable equilibrium conditions for the profiles, which enter the determination of $\Delta\Omega_u$, the excess thermodynamic potential for a "uniform phase" characterized by given values of η and $\mu_{\mathbf{G}}$, and given basically by eqn. (6).

The authors briefly discuss also the case of a spherical solid particle in its own liquid and point out the relevance of such a model to calculations of the rate of solid phase nucleation in liquids.

3.5 Structure of the solid-liquid interface and crystal-growth mechanisms

The question of the structure of the solid-liquid interface, in dependence of the material and of thermodynamic conditions, is of great importance in the discussion of crystal growth mechanisms. It is clear that an interface which has an atomically smooth equilibrium configuration will advance into the liquid by successive processes of two-dimensional nucleation of new atomic layers, whereas a rough interface, in which several atomic layers are involved in the transition zone, has a large number of suitable sites at which new atoms can be continuously accomodated. The equilibrium structure of the interface will thus influence the kinetics of the growth process, at least if the rate of motion of the atoms over the interface is sufficiently fast relative to the rate of growth that such equilibrium structure can be maintained during crystal growth.

For a rather complete discussion of these problems the book of Woodruff[3] should be referred to. The leading works in this area are the discussion of the free solid surface by Burton, Cabrera and Frank[43] and its simplified extension to the solid-liquid interface by Jackson[44], that we proceed to summarize.

Jackson's treatment of a system of adatoms on a surface is equivalent to a Bragg-Williams theory of a two-level system. The free energy change ΔG associated with randomly adding N_A atoms is being considered at the equilibrium temperature T_m for the phase change, on the assumption that $P\Delta V$ in the solid-liquid transition is negligible. An energy change ΔE arises from the interactions of the adatoms with the substrate and with each other, and is written as

$$\Delta E = -N_A\left[2L\frac{n_0}{n} + L\frac{n_1}{n}\frac{N_A}{N}\right] \qquad (12)$$

where L is the latent heat of melting, N is the number of atoms in a complete adlayer, n_0 and n_1 are structural coefficients giving the numbers of first-neighbors to the adatom in the substrate and in the adlayer, and $n=2n_0+n_1$ is the number of first neighbours in the bulk solid (the Bragg-Williams approximation enters the adatom-adatom term). An entropy term arises both from the transfer of adatoms from liquid to solid and from configurational disorder in the adlayer,

$$\Delta S = -\frac{L}{T_m}N_A + k_B \ln\left[\frac{N!}{N_A!\,(N-N_A)!}\right] \qquad (13)$$

Using the Stirling formula ($\ln N! \simeq N\ln N - N$) one thus has

$$\frac{\Delta G}{Nk_BT_m} = \alpha N_A \frac{N-N_A}{N^2} - \ln\frac{N}{N-N_A} - \frac{N_A}{N}\ln\frac{N-N_A}{N_A} \qquad (14)$$

where $\alpha = \frac{n_1}{n}\frac{L}{k_BT_m}$. This expression for ΔG must be minimized with respect to N_A/N to find the equilibrium structure of the adlayer, which in this simple theory represents the transition region between solid and liquid.

Two different types of behaviour are found in different ranges of values for the parameter α. For $\alpha<2$ the minimum of ΔG lies at $N_A/N = 1/2$, which corresponds to a completely rough interface. If $\alpha>2$, on the other hand, there is a maximum of ΔG at $N_A/N = 1/2$ but minima occur for $N_A/N \simeq 0$ and $N_A/N \simeq 1$: the equilibrium state thus is an atomically smooth surface. The parameter α essentially measures the entropy of melting, and there is a good correlation between these predictions of this simple theory and observation: high-α materials grow with a faceted habit whereas low-α materials (typically but not exclusively metals) tend to show dendritic growth, especially at high supercooling. The sharp transition between these two modes of behaviour is however an artifact of the simplified treatment, and intermediate cases are known of systems (such as Bi) which can show both modes of growth.

A generalization of this model has been given by Temkin[45] to allow for a multiplicity of layers in the interfacial transition region – in fact the number of layers involved is kept as a variable which can adjust itself to minimize the free energy. The partition function of the system is written as a function of the numbers N_n of "solid-like" atoms in the various layers and the free energy of the system, evaluated in the Bragg-Williams approximation (i.e. by taking $\langle N_{ls}^{(n)}\rangle = n_1 N_n \left(1-\frac{N_n}{N}\right)$ for the average number of liquid-solid bonds in the n-th layer) is numerically minimized with respect to these variables. The excess free energy of a random configuration over that of a smooth boundary has the form (for a s c lattice)

$$\frac{\Delta G}{N k_B T} = \frac{\Delta\mu}{k_B T}\left[\sum_{n=-\infty}^{0}\left(1-\frac{N_n}{N}\right) - \sum_{n=1}^{\infty}\frac{N_n}{N}\right] + \frac{4w}{k_B T}\sum_{n=-\infty}^{\infty}\frac{N_n}{N}\left(1-\frac{N_n}{N}\right) + \sum_{n=-\infty}^{\infty}\frac{N_{n-1}-N_n}{N}\ln\frac{N_{n-1}-N_n}{N} \qquad (15)$$

and the equilibrium conditions are

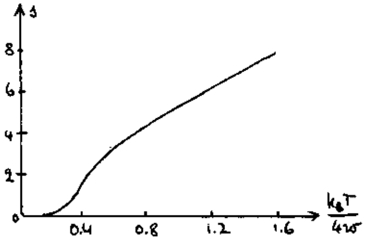
$$\frac{N_n - N_{n+1}}{N_{n-1}-N_n}\exp\left(\frac{8w}{k_B T}\frac{N_n}{N}\right) = \exp\left(\frac{\Delta\mu - 4w}{k_B T}\right). \qquad (16)$$

Here $\Delta\mu$ is the difference in chemical potentials between atoms in the two phases (essentially $\Delta\mu \propto L\,\Delta T/T_m$ in terms of the latent heat of melting and of the supercooling) while $w = \varepsilon_{ls} - \frac{1}{2}(\varepsilon_{ss}+\varepsilon_{ll})$ with ε_{ls} = bond energy between a "solid-like" and a "liquid-like" atom etc. Eqn (15) can be shown to reduce to Jackson's equation in the appropriate limit (with $\alpha = 4w/k_B T_m$).

In the case $\Delta\mu = 0$ (i.e. $T = T_m$) the surface roughness parameter s, defined by

$$s = 4\sum_{n=-\infty}^{\infty}\frac{N_n}{N}\left(1-\frac{N_n}{N}\right), \qquad (17)$$

is found to have the behaviour indicated in the sketch: the sharp transition from a rough surface to a smooth surface is seen to be removed. Furthermore, in such an equilibrium situation the mean position of the interface is fixed relative to the lattice periodicity to lie midway between the n=0 and n=1 layers. A sinusoidal-like succession of free-energy barriers thus has to be surmounted to advance the mean position of the interface into the liquid (or into the solid).



In the case of a supercooled liquid, a driving force for surmounting these barriers is provided by the chemical potential difference $\Delta\mu$. In dependence from the values of $\Delta\mu$ and w, two different crystal-growth behaviours are then indicated by the theory. If w is sufficiently large and/or the supercooling is still moderate, one still finds an equilibrium solution for eqns (16), implying that a free energy barrier still exists for crystal growth: two-dimensional nucleation and screw dislocation mechanisms must intervene. No equilibrium solution is found instead if $\Delta\mu$ is large or w is small: a continuous, barrier-less growth mechanism is then indicated. This second type of mechanism can be estimated to be operative for metals already at supercoolings of the order of 10^{-2} degrees. For a good discussion of the difficulties involved in experiments on growth kinetics, the book of Woodruff[9] is again recommended.

The parameter w measures the solid-liquid interfacial free energy γ_{sl} and is of the order of the latent heat of melting per atom (see also §1.4). Important parameters for the kinetics of crystal growth are the interfacial thickness, the interface being sharper for higher-γ_{sl} materials, and of course the supercooling, expressed through the difference in chemical potentials between the two phases. Molecular theories of the interface can usefully contribute by giving a microscopic basis for these simple theories.

4. Electrified interfaces

4.1 The electrical double layer

We have stressed in the introductory chapter the anisotropic nature of the internal forces acting on the particles near the boundary of a finite system or at an interphase boundary. In a system consisting of mobile charged particles (e.g. a molten salt) this anisotropy will in general result in a redistribution of charges near the boundary, relative to their distribution in the bulk, and thus in the creation of an electrical double layer and a potential drop across the interface. As we noted in §25 on metals, separation of the electronic and ionic density profiles is allowed for in more refined theories – this effect contributes to determining the electronic work function of the metal. The argument is in fact so general that we should expect an electrical double layer to arise at an interphase boundary even if the material does not contain free charges but consists of molecules with permanent dipoles or of molecules in which dipoles can be induced.

A specific example of great practical importance, on which we shall here focus, is the case of a liquid electrolyte (salt dissolved in water, say) in contact with a metallic electrode. Orientation of water dipoles and redistribution of positive and negative ion densities occur in the interface region. These rearrangements can produce a net charge on the electrolyte side of the interface if a compensating charge is induced on the electrode side of the interface, essentially by a redistribution of the conduction electrons relative to the ionic lattice. A double layer and a potential drop have thus been created across the interface. Although the potential difference is not large (typically of the order of a Volt) the field strength in the interface region, with a typical thickness of 10 Å, is enormous.

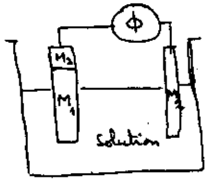
Our microscopic understanding of such a basic problem is still in a rather primitive stage, as we can easily realize if we look in some qualitative detail at the double layer. Starting from the electrode side of the interface, we should ask about the electronic surface properties of a metal in contact with an electrolyte and the effects of the surface structure of the metal. Just across the metal surface we meet a hydration sheath of oriented water molecules, possibly including some adsorbed ions from the dissolved salt. There follows a screening cloud of hydrated ions, tapering off into the homogeneous bulk solution. At the simplest macroscopic level this distribution of charges and dipoles may be schematized as a capacitor, whose plates are the metal surface (carrying a charge q per unit area, say) and the "outer Helmholtz plane" where the ionic charges in the electrolyte (of

total amount $-q$ per unit area) are thought to be concentrated. It is clear that the capacitance of the interface is the result of rather complex microscopic physics. Still remaining at the macroscopic level, the potential profile for the above model (which is a linear variation with distance from the metal surface to the outer Helmholtz plane) has to be modified to allow for ionic adsorption and for a finite extent of the screening cloud: a nontrivial dependence of the (differentially defined) capacitance on applied voltage will result even if the solvent is still thought of as a uniform dielectric.

The following discussion is meant as an introduction to some basic aspects of this field, while a progress report will be given later in the lectures of Prof. Rickayzen. For a more detailed introduction reff. 46 and 47 are very useful.

4.2 Thermodynamics of interfacial region

- The first point that we need to discuss is how can one experimentally isolate the potential difference across the electrode-electrolyte interface. The scheme of the experimental arrangement is shown in the adjoining sketch: by Kirchhoff's second law the potential difference ϕ at the measuring instrument is related to the potential differences at the various interfaces ($\phi_{M_1/S}$ between the electrode M_1 under study and the solution, ϕ_{M_2/M_1} between M_1 and the metal M_2 of the second electrode, and ϕ_{S/M_2}) by



$$\phi = \phi_{M_1/S} + \phi_{M_2/M_1} + \phi_{S/M_2} . \qquad (1)$$

On changing the external potential, the contact potential ϕ_{M_2/M_1} between the two metals remains constant, and the change in $\phi_{M_1/S}$ can be isolated if (i) M_1 is a "polarizable" (or "blocking") electrode, and (ii) M_2 is a "non-polarizable" (or "reversible") electrode. These two ideal opposite-type electrodes correspond, respectively, to the case where no charges can leak across the interface and to the case where the resistance to charge flow is essentially zero. In such an ideal situation (which can be realised to a high degree in the laboratory) the potential difference ϕ_{S/M_2} also remains constant on changing ϕ, and hence

$$d\phi = d\phi_{M_1/S} . \qquad (2)$$

Thus while $\phi_{M_1/S}$ cannot be measured absolutely, its change $d\phi_{M_1/S}$ has a direct meaning as a differential quantity to be used in a thermodynamic description of the interface.

To introduce such a description let us consider the simple case of a 1:1 electrolyte in contact with an ideal polarizable electrode (a general discussion is given by R. Parsons in ref. 47). We write the differential of the internal energy U as

$$dU = TdS - PdV + \gamma dA + \sum_{\alpha=1}^{2} \bar{\mu}_\alpha dN_\alpha \tag{3}$$

where γ is the interfacial tension (measurable by electrocapillary techniques: see ref. 46) and $\bar{\mu}_\alpha$ are the electrochemical potentials of the two ionic species in the solution. On comparing eqn (3) with the corresponding expression for the bulk electrolyte, we isolate the interfacial excesses (denoted by the superscript σ)

$$dU^\sigma = TdS^\sigma - PdV^\sigma + \gamma dA + \sum_\alpha \mu_\alpha dN_\alpha^\sigma + \phi_{M/S} dQ \tag{4}$$

where we have written $\bar{\mu}_\alpha = \mu_\alpha - Z_\alpha e \phi_{M/S}$ in terms of the chemical potentials μ_α in the bulk and of valences Z_α (with $|Z_\alpha| = 1$), and have used the overall neutrality condition of the interface,

$$\sum_\alpha Z_\alpha e N_\alpha^\sigma = -Q \tag{5}$$

to relate the excess charge in the electrolyte to the charge Q on the electrode. On integrating eqn (4) over the extensive variables, at fixed values of the intensive variables, we get

$$U^\sigma = TS^\sigma - PV^\sigma + \gamma A + \sum_\alpha \mu_\alpha N_\alpha^\sigma + \phi_{M/S} Q \tag{6}$$

which upon differentiation and comparison with (4) yields the Gibbs adsorption equation,

$$d\gamma = -s\,dT + v\,dP - \sum_\alpha n_\alpha d\mu_\alpha - q\, d\phi_{M/S}. \tag{7}$$

The quantities s, v, n_α and q are now interfacial excess quantities per unit area. From eqn (1) we have

$$d\phi_{M/S} = d\phi - d\phi_{S/M_2} \tag{8}$$

and, if the reference electrode is reversible to the ionic species $\alpha = 2$ (say), we have also

$$d(\mu_2 + Z_2 e \phi_{S/M_2}) = 0. \tag{9}$$

Hence, at constant temperature and pressure, eqn (7) becomes

$$d\gamma = -q\, d\phi - n_1 d\mu \qquad (\mu = \mu_1 + \mu_2) \tag{10}$$

which is the desired basic thermodynamic relation.

From this relation it follows that

$$q = -\left(\frac{\partial \gamma}{\partial \phi}\right)_\mu \tag{11}$$

and hence one gets a thermodynamic definition for the interfacial capacitance C (originally due to Lippmann, 1875)

$$C \equiv \left(\frac{\partial q}{\partial \phi}\right)_\mu = -\left(\frac{\partial^2 \gamma}{\partial \phi^2}\right)_\mu . \tag{12}$$

Furthermore, the interfacial excess of the "non-reversible" species is given by

$$n_1 = -\left(\frac{\partial \gamma}{\partial \mu}\right)_\phi . \tag{13}$$

Thus the differential capacitance can be determined from the dependence of the interfacial tension on applied potential at fixed composition of the solution, and the surface excess can be determined from the dependence of the interfacial tension on composition ([illegible] on the "activity" of the solution) at constant applied potential.

γ as a function of ϕ is found to have a maximum, which defines a fundamental reference potential for the electrified interface (the potential of zero charge: see eqn (11)). At this point the potential drop across the interface is determined purely by polarization processes. The shape of γ vs ϕ is roughly an inverted, somewhat asymmetric parabola. Some examples of experimental data, taken from the article of R. Reeves in ref. 47, are reproduced below.

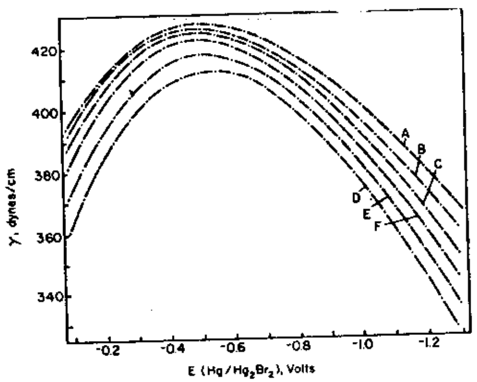


Figure 2. Electrocapillary curves for the mercury–aqueous KBr interface. Concentration of KBr solution (A) 0.01 F, (B) 0.03 F, (C) 0.1 F, (D) 0.3 F, (E) 1.0 F, (F) 3.0 F. E vs. Hg/Hg_2Br_2 electrode.(81)

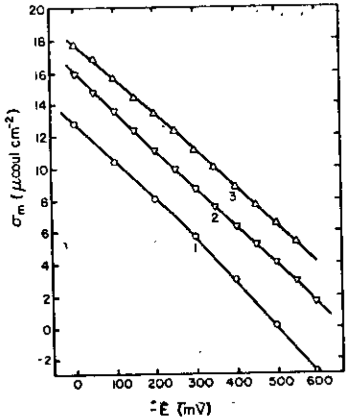


Figure 3. Charge–potential curves at constant values of adsorbed $Cr(OH_2)_3(NCS)_3$. (1) 1 M NaClO–0.01 M $HClO_4$, $T = 0$; (2) same electrolyte but $I = 1.25 \times 10^{-10}$ mol cm^{-2}; (3) same electrolyte but $T = 2.1 \times 10^{-10}$ mol cm^{-2}. The charges were obtained from coulostatic and potentiostatic steps from -100 mV.(73)

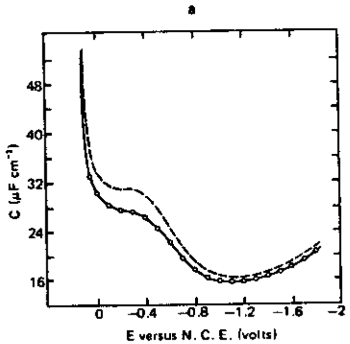


Figure 4.(a) Differential capacity of mercury in 0.916 M sodium fluoride at 25°C. Dashed line represents the differential capacity C_{M-2} of the compact double layer.(62)

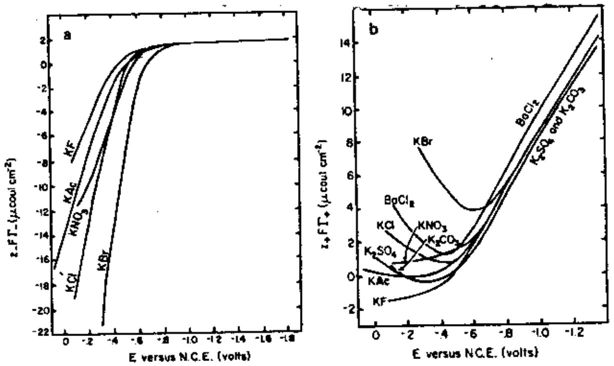


Figure 6. (a) Relative (to water) surface excesses of anions. (b) Relative (to water) surface excess of cations. All data for 0.1 M solutions of electrolytes at 25°C on mercury. Surface excess expressed as a charge.(64)

4.3 The Gouy-Chapman-Stern model

A simple model for an electrode-electrolyte interface was introduced a long time ago by Gouy[48] and Chapman[49]: the model considers a fluid of point ions in a uniform dielectric medium, which builds up a diffuse layer of screening charge in front of a charged hard wall. We go in some detail through this model because it is the prototype of self-consistent theories of charged-particles fluids, self-consistency being imposed by the long-range nature of the Coulomb interactions. The best known simple example of such theories is the Debye-Hückel theory for bulk electrolytes, which was actually preceded in time by the GC development. The following discussion will thus serve also as an introduction to the lectures on charged fluids to be delivered later by Prof. Hansen.

In the GC theory the approximation is made that the particle densities $n_\alpha(z)$ are simply related to the electric potential energy $\phi(z)$ by a Boltzmann-distribution expression,

$$n_\alpha(z) = n_\alpha^0 \exp\left[-Z_\alpha \phi(z)/k_BT\right], \qquad (14)$$

as for a system of non-interacting particles in an external potential.[+] n_α^0 are the particle densities in the bulk electrolyte, where we have chosen $\phi(\infty)=0$. Self-consistency is introduced by requiring that $\phi(z)$ be determined both by the charge on the wall and by the charge density $n_Q(z) = \sum_\alpha Z_\alpha e\, n_\alpha(z)$ induced in the electrolyte (the whole being screened by the dielectric constant ε of the uniform medium which represents the solvent). Thus $\phi(z)$ satisfies the Poisson equation

$$\begin{aligned}\frac{d^2\phi(z)}{dz^2} &= -\frac{4\pi e}{\varepsilon}\, n_Q(z) \\ &= -\frac{4\pi e^2}{\varepsilon}\sum_\alpha Z_\alpha n_\alpha^0 \exp\left[-Z_\alpha\phi(z)/k_BT\right] \qquad (z>0)\end{aligned} \qquad (15)$$

with the boundary condition (following from Gauss' theorem)

$$q = -\frac{\varepsilon}{4\pi e}\left(\frac{d\phi(z)}{dz}\right)_{z=0}. \qquad (16)$$

For a 1:1 electrolyte (where $|Z_\alpha|=1$ and $n_1^0 = n_2^0 = n_0$, say), with the relation $\frac{d}{dz}\left(\frac{d\phi}{dz}\right)^2 = 2\frac{d\phi}{dz}\frac{d^2\phi}{dz^2}$ one obtains a first integral of eqn. (15) as

$$-\frac{d\phi(z)}{dz} \equiv eE(z) = \left(\frac{32\pi k_BT n_0 e^2}{\varepsilon}\right)^{1/2}\sinh\frac{\phi(z)}{2k_BT} \qquad (17)$$

where $E(z)$ is the electric field; the integration constant has been chosen so that the field vanishes in the bulk electrolyte and the sign has been chosen through consistency between the sign of the wall charge and the signs of the potential and the field. Further integration of eqn (17) yields

$$\phi(z) = 4k_BT\, \mathrm{tgh}^{-1}\left(s\, e^{-\kappa z}\right) \qquad (18)$$

where $s \equiv \mathrm{tgh}\left(\frac{\phi(0)}{4k_BT}\right)$ and $\kappa = \left(\frac{8\pi n_0 e^2}{\varepsilon k_BT}\right)^{1/2}$ is the Debye-Hückel inverse screening length. This result corresponds to an approximately exponential decay of $\phi(z)$, as can be seen in the case where s is small, $\phi(z) \simeq \phi(0)e^{-\kappa z}$.

The surface charge density on the wall is related to $\phi(0)$ by eqn (16),

$$q = \left(\frac{2k_BT\varepsilon n_0}{\pi}\right)^{1/2}\sinh\frac{\phi(0)}{2k_BT}. \qquad (19)$$

We should now identify $\phi(0)$ with $e\phi_{M/S}$ in the preceding section: from eqn (7) at constant T, P and chemical potentials we get the capacitance C_d of the diffuse layer as

$$C_d = e\left(\frac{\partial q}{\partial\phi(0)}\right)_{\text{composition}} = \left(\frac{\varepsilon n_0 e^2}{2\pi k_BT}\right)^{1/2}\cosh\frac{\phi(0)}{2k_BT}. \qquad (20)$$

This yields $C_d = \frac{\varepsilon}{4\pi}\kappa$ at the point of zero charge, followed by an initially parabolic rise with voltage. The surface excess of particles of either species can also be calculated (for $Z_\alpha = \pm1$) as

$$\begin{aligned} n_\alpha &= \int_0^\infty dz\left[n_\alpha(z) - n_\alpha^0\right] = n_0\int_0^\infty dz\left[e^{-Z_\alpha\phi(z)/k_BT} - 1\right] \\ &= 2n_0 Z_\alpha \int_0^\infty dz\; e^{-Z_\alpha\phi(z)/2k_BT}\,\frac{d\phi(z)}{dz}\left(\frac{32\pi k_BT n_0 e^2}{\varepsilon}\right)^{-1/2} \\ &= \left(\frac{\varepsilon k_BT n_0}{2\pi e^2}\right)^{1/2}\left[e^{-Z_\alpha\phi(0)/2k_BT} - 1\right], \end{aligned} \qquad (21)$$

the last step involving a change from an integral over z to an integral over ϕ. Finally the interfacial tension (relative to its value at the potential of zero charge) is easily evaluated by integration of (19) and (21) with the thermodynamic relations of the preceding section:

$$\gamma = -2k_BT\left(\frac{2k_BT\varepsilon n_0}{\pi e^2}\right)^{1/2}\left[\cosh\left(\frac{\phi(0)}{2k_BT}\right) - 1\right]. \qquad (22)$$

This corresponds to setting[+]

$$\gamma = -\frac{\varepsilon}{4\pi}\int_0^\infty dz\, E^2(z). \qquad (23)$$

Notice also that the chemical potentials μ_α in this theory are taken to have the free-particle value $\mu_\alpha = k_BT\ln\left[n_0\left(\frac{2\pi\hbar^2}{Mk_BT}\right)^{3/2}\right]$.

In applying the results of the GC diffuse-layer theory to an analysis of experimental data on electrode-electrolyte interfaces, it has become customary following Stern[51] to recognize that, in addition to the diffuse-layer contribution C_d, a second so-called "inner layer" contribution C_i is present. In the simplest viewpoint, this accounts for finite ionic sizes by allowing for a minimum non-vanishing value of the distance of closest approach of the ions to the wall (i.e. the position z=0 in the above discussion should represent the position of the "outer Helmholtz plane", at a distance from the wall which is of the order of the radius of hydrated ions), rather than the edge of the wall). The interface is then

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[+] This approximation is fully analogous to that made in the Debye-Hückel theory: there one considers the particle densities surrounding a given ion rather than those in front of a charged hard wall. The wall can in fact be thought of as an ion with a very large radius and a given amount of surface charge density.

[+] Eqn (23) follows in general[50] for a charged-particles fluid when the density-gradient expansion of §2.4 is truncated at its leading term, i.e. in a local-density approximation.

viewed as a series of two capacitors,

$$C = \left(\frac{1}{C_i} + \frac{1}{C_d}\right)^{-1} . \tag{24}$$

Some such assumption is necessary to make contact with the experiments, at least if one presumes that the GC theory provides a reasonable account of the diffuse layer: indeed C_d is found to become much larger than the measured capacitance when the solute concentration or the applied potential increase, and eqn (24) will then instead imply that C_d becomes irrelevant in such conditions. Conversely this implies that except in special conditions (low concentrations and applied potentials near the point of zero charge) it is difficult to test the GC theory against experiment. Various tests have nevertheless been devised: for a discussion see the article of R. Reeves in ref. 47.

Much effort has been devoted to modelling the inner layer - the GC theory being often used to isolate the corresponding capacitance on the assumption that eqn (24) holds. We simply mention here some of the problems that have been discussed, with some recent references:

(i) models of the dipolar orientation contribution in the inner layer and effects of dielectric saturation (see e.g. the article of Reeves in ref. 47, and ref. 52);

(ii) preferential adsorption of ions and solvent molecules at the electrode, implying a multiplicity of Stern layers (see e.g. the article of Habib and Bockris in ref. 47);

(iii) non-local effects in dielectric screening and spilling out of the electron distribution from the electrode (see e.g. ref. 53);

(iv) improved theories of the ionic screening cloud (see e.g. reff. 54 and 55).

The application of computer simulation techniques should prove useful in this area, as in other areas of interfacial physics.

As a contribution to the statistical mechanics of interfaces, we would also like to mention the exact solution recently obtained[56] for the one-body density in a two-dimensional classical plasma enclosed in a circular box.

References

1. J.W. Cahn and J.E. Hilliard, J. Chem. Phys. 28, 258 (1958).
2. T.E. Faber, "An Introduction to the Theory of Liquid Metals" (Cambridge University Press, 1973).
3. P.A. Egelstaff and B. Widom, J. Chem. Phys. 53, 2667 (1970).
4. B. Widom, J. Chem. Phys. 43, 3892 (1965).
5. A.B. Bhatia and N.H. March, J. Chem. Phys. 68, 4651 (1978).
6. F.P. Buff and R.A. Lovett, in "Simple Dense Fluids" (Academic Press, New York 1968).
7. D. Turnbull, J. Chem. Phys. 18, 768 (1950) and J. Appl. Phys. 21, 1022 (1950).
8. C. Herring, in "The Physics of Powder Metallurgy" (McGraw-Hill, New York 1951).
9. D.P. Woodruff, "The Solid-Liquid Interface" (Cambridge University Press, 1973).
10. The original paper of van der Waals, published in 1893, has been translated into English by J.S. Rowlinson, J. Stat. Phys. 20, 197 (1979).
11. J.G. Kirkwood and F. Buff, J. Chem. Phys. 17, 338 (1949).
12. D.G. Triezenberg and R. Zwanzig, Phys. Rev. Letters 28, 1183 (1972).
13. R. Evans, Adv. Phys. 28, 143 (1979).
14. R.H. Fowler, Proc. Roy. Soc. A159, 229 (1937).
15. I.R. McDonald and K.S.C. Freeman, Molec. Phys. 26, 529 (1973).
16. M.V. Berry, in "Surface Science" vol. 1 (IAEA, Vienna 1975).
17. P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); N.D. Mermin, Phys. Rev. 137, A1441 (1965); W. Kohn and L.J. Sham, Phys. Rev. 140, A1133 (1965).
18. A.J.M. Yang, P.D. Fleming and J.H. Gibbs, J. Chem. Phys. 64, 3732 (1976).
19. A.B. Bhatia and N.H. March, J. Chem. Phys. 68, 1999 (1978).
20. P.D. Fleming, A.J.M. Yang and J.H. Gibbs, J. Chem. Phys. 65, 7 (1976); A.B. Bhatia, N.H. March and M.P. Tosi, Phys. Chem. Liquids 9, 229 (1980); G. Senatore and M.P. Tosi, N. Cimento 56B, 169 (1980).
21. R.C. Brown and N.H. March, J. Phys. C6, L363 (1973).
22. C.F. von Weizsäcker, Zs. Phys. 96, 431 (1935); D.A. Kirznits, Sov. Phys. JETP 5, 64 (1957).
23. N.D. Lang and W. Kohn, Phys. Rev. B1, 4555 (1970) and B3, 1215 (1971); N.D. Lang, Solid State Physics 28, 225 (1973); see also K.S. Singwi and M.P. Tosi, Solid State Physics 36, 177 (1981).
24. J.A. Appelbaum and D.R. Hamann, Revs. Mod. Phys. 48, 479 (1976).
25. W. Kohn and A. Yaniv, Phys. Rev. B20, 4948 (1979).
26. K.S. Singwi and M.P. Tosi, Phys. Rev. B23, 1640 (1981).
27. A.R. Ubbelohde, "The Molten State of Matter" (Wiley, New York 1978).
28. G. Navascues, Repts. Progr. Phys. 42, 1131 (1979).

29. T.V. Ramakrishnan and M. Yussouff, Solid State Commun. 21, 389 (1977) and Phys. Rev. B19, 2775 (1979).
30. N.H. March and M.P. Tosi, Phys. Chem. Liquids 11, 79 and 89 (1981).
31. S.F. Edwards and M. Warner, Phil. Mag. A40, 257 (1979).
32. J.P. Hansen and L. Verlet, Phys. Rev. 184, 150 (1969).
33. D.K. Chaturvedi, G. Senatore and M.P. Tosi, Lett. N. Cimento 30, 47 (1981).
34. A. Ferraz and N.H. March, Solid State Commun. 36, 977 (1980).
35. N.H. March and M.P. Tosi, Phys. Chem. Liquids 11, 129 (1981).
36. A.B. Bhatia and D.E. Thornton, Phys. Rev. B2, 3004 (1970).
37. M. Parrinello and M.P. Tosi, Riv. N. Cimento 2, no. 6 (1979).
38. H. Reiss, S.W. Mayer and J.L. Katz, J. Chem. Phys. 35, 820 (1961).
39. N.H. March and M.P. Tosi, Phys. Chem. Liquids 10, 185 (1980).
40. M. Rovere, N.H. March and M.P. Tosi, to be published.
41. F.R.N. Nabarro, "Theory of Crystal Dislocations" (Clarendon Press, Oxford 1967); see also D. Kuhlmann-Wilsdorf, Phys. Rev. 140, A1599 (1965).
42. A.D.J. Haymet and D.W. Oxtoby, J. Chem. Phys. 74, 2559 (1981).
43. W.K. Burton, N. Cabrera and F.C. Frank, Phil. Trans. Roy. Soc. A243, 299 (1951).
44. K.A. Jackson, "Liquid Metals and Solidification" (ASM, Cleveland 1959).
45. D.E. Temkin, "Crystallisation Processes" (Consultants Bureau, New York 1966).
46. J. O'M. Bockris and A.K.N. Reddy, "Modern Electrochemistry" (Plenum Press, New York 1977).
47. J. O'M. Bockris, B.E. Conway and E. Yeager (editors), "Comprehensive Treatise of Electrochemistry 1: The Double Layer" (Plenum Press, New York 1980).
48. G. Gouy, J. Chim. Phys. (Paris) 29, 145 (1903) and J. Phys. (Paris) 9, 457 (1910).
49. D.L. Chapman, Phil. Mag 25, 475 (1913).
50. G. Senatore and M.P. Tosi, N. Cimento B56, 169 (1980).
51. O. Stern, Zs. Elektrochem. 30, 508 (1924).
52. S.H. Liu, Surface Sci. 101, 49 (1980).
53. A.A. Kornyshev and M.A. Vorotyntsev, Surface Sci. 101, 23 (1980).
54. S. Levine and C.W. Outhwaite, JCS Faraday II, 74, 1670 (1978); S. Levine, C.W. Outhwaite and L.B. Bhuiyan, J. Electroanal. Chem. 123, 105 (1981).
55. L. Blum, J. Phys. Chem. 81, 136 (1977).
56. B. Jancovici, J. Phys. Lettr. 42, L223 (1981).