SURFACES.THE SURFACE PROPERTIES OF LIQUID METALS

R. Evans

SURFACES.——

THE SURFACE PROPERTIES OF LIQUID METALS

R. Evans

H.H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, U.K.

Abstract.- We briefly review recent theoretical and experimental work on the surfaces of various liquids and liquid mixtures. While there has been much progress in understanding the surface structure and thermodynamic properties of argon-like liquids and molten salts, the surface properties of liquid metals and their alloys are much less understood. We mention the relevance of the studies of other liquids to liquid metal surfaces and describe some outstanding problems in this area.

1. Introduction

In recent years there has been considerable progress in understanding the bulk thermodynamics and structure of many liquid metals and their alloys. Accurate neutron and X-ray diffraction experiments have been a stimulus for detailed microscopic modelling of the structure factors and radial distribution functions. For simple (non-transition or rare-earth) metals it is possible to calculate interionic potentials using pseudopotential theory to describe the electron-ion interaction and these effective pairwise potentials give a rather good description of the observed structure and several thermodynamic properties e.g. (1, 2, 3). For transition and rare-earth metals and their alloys the situation is less satisfactory, since for these systems the electron-ion interaction is strong and cannot be modelled by a weak pseudopotential. Consequently there is no tractable theory for interionic forces in these metals. Nevertheless it is known that the structure factors of many pure transition metals can be crudely modelled by hard-spheres of the appropriate diameter (4) and some understanding of the entropy (5) has emerged. By contrast the surfaces of liquid metals are much less studied and are certainly not well-understood. There is a wealth of experimental data on the liquid-vapour surface tension γ for both pure metals and alloys (6, 7) since a knowledge of this interfacial quantity is important in many practical and technological applications of liquid metals. However, even the magnitude of γ and its variation from metallic element to element through the periodic table is not satisfactorily explained by existing theories. When we examine another important interfacial quantity, the liquid-solid surface tension, the situation is much worse;

there are few reliable experimental determinations and there is essentially no theory. This means that there is no basis for a microscopic description of angle of contact, wetting properties etc., which are crucial for many metallurgical processes. In binary alloys there is an important extra feature associated with the presence of an interface and this concerns the surface concentrations of the two constituents. Many liquid alloys are known to exhibit the phenomenon of surface segregation, i.e. the concentrations of the components in the interfacial region are significantly different from those in the bulk liquid. This phenomenon gives rise to pronounced effects in the concentration dependence of the surface tension of the alloy (7) and is important for surface chemistry since the behaviour of adsorbed species depends strongly on the nature of the surface 'layers'. The basic factors which determine segregation in alloys are not well-understood from a microscopic viewpoint.

One of the main reasons for lack of progress in this general area is the absence of any direct experimental probe of the surface structure; there is nothing comparable to the diffraction data which has played a key role in the understanding and development of theory for bulk liquids. Indeed there appears to be only one measurement, an estimate of the surface 'thickness' of the liquid-vapour interface of Hg (8) obtained by an X-ray technique, which gives some direct information on the interfacial structure. There are several experiments which yield interesting and useful indirect information concerning interfacial structure. The surface tension γ is a surface excess thermodynamic property and therefore depends on the ionic and electron density profiles in the interface; more specifically it involves

integrations over these interfacial profiles. Similarly the temperature coefficient of the surface tension $\partial\gamma/\partial T$, which is a measure of the surface excess entropy i.e. the extra disorder introduced by having an interface, is an integral quantity. The work function depends on the electronic structure of the interface via the total electrostatic potential difference, the dipole barrier (9). It is interesting that the work function for many simple metals shows almost no change at the melting transition (10) indicating that the dipole barrier at the liquid metal surface should be very similar to that of the polycrystalline solid. This behaviour appears somewhat surprising when one notes that the work function of crystalline metals often varies by about 10% between different surfaces of the same single crystal (9, 11). Another indirect experiment, which is not usually regarded as a surface probe but can be very useful for studying surface segregation in liquid (and solid) alloys, is photoelectron spectroscopy. In favourable systems it is possible to estimate the effective surface concentration of each species by measuring the relative intensities of prominent electronic structures, e.g. d band features, associated with the individual species. Segregation has been investigated in several binary alloys (10) using photoemission.

While progress in understanding the surfaces of other liquids has also suffered from a lack of microscopic information concerning the interfacial structure, theory has been making some headway over the last decade. Consequently it is reasonable to ask whether the theoretical expertise which has been successfully developed for other liquid systems might be useful for elucidating the surface structure and properties of liquid metals. In this article we briefly describe the results of some recent theoretical work and computer simulations on the surfaces of pure, monatomic, insulating (argon-like) liquids, mixtures of argon-like liquids and molten salts. We will mention the relevance of these studies to liquid metal surfaces and discuss the current state of the theory for metals. Throughout we concentrate on the liquid-vapour interface at low temperatures (near the triple point) since this is the problem which has received most attention.

2. Pure Monatomic Liquids

It is probably safe to argue that the liquid-vapour interface of pure argon-like fluids, over the full-range of liquid-vapour coexistence, is now well-understood; for recent reviews see (12, 13, 14). The surface tension, the form of the atomic density profile and even the pairwise distribution function have been investigated using a variety of theoretical techniques and in Monte Carlo and molecular dynamics simulations. The basic theoretical problem is how to solve the classical equilibrium statistical mechanics for an extremely inhomogeneous fluid; near the triple point the density varies by several orders of magnitude, from the bulk liquid to the bulk vapour, over a distance of a few $\overset{\circ}{A}$. Theory and simulation predict monotonic profiles whose widths increase smoothly with temperature, diverging at the critical temperature. Near the triple point the '10-90' thickness of the interface, defined as the distance over which the density changes from 0.9 $(\rho_\ell - \rho_v)$ to 0.1 $(\rho_\ell - \rho_v)$ where ρ_ℓ and ρ_v are the bulk liquid and vapour densities, is predicted to be about 2 molecular diameters. This is in good agreement with the result of a recent optical reflectivity (ellipsometry) measurement on liquid Ar (15). The values of the surface tension obtained from various theories are in reasonable agreement with computer results and give a rather good description of the measured surface tension of Ar.

Most of the recent theoretical work is based on a density functional approach (12). The simplest theory expands the free energy of the inhomogeneous fluid as a series of density gradients and makes a proper microscopic identification of the coefficients. If this series is truncated at the square-gradient term the resultant theory for the surface tension and density profile is of the same form as the classic van der Waals (16) theory. Calculations based on this approach give a very good qualitative and reasonable quantitative account of computer and experimental results (17).

Current theoretical and computational effort is focussed on the nature of pairwise correlations in the interface (12). General theoretical arguments predict that the pairwise distribution function $\rho^{(2)}(\underline{r}_1,\underline{r}_2)$ should exhibit long-ranged (macroscopic) correlations parallel to the

interface when the z coordinates of the particles, z_1 and z_2, lie in the interface. The correlation length is given by

$$\zeta = \left[\gamma/(\rho_\ell - \rho_v)mg \right]^{\frac{1}{2}} \qquad (1)$$

which diverges as g, the acceleration due to gravity, goes to zero. γ is the surface tension. Computer studies [18] of the pairwise distribution function seem to confirm the existence of such correlations but a detailed microscopic model is still lacking.

3. Mixtures of Simple Liquids

There has been relatively little attention devoted to the statistical mechanical description of the liquid-vapour interface of classical multi-component systems; consequently the large amount of experimental data on the concentration dependence of the surface tension and its implication for surface segregation lacks a detailed explanation. As a first step towards a microscopic treatment of such interfaces Telo da Gama and Evans [19] have recently carried out detailed calculations of the density profiles and surface tension for binary mixtures of Lennard-Jones fluids using a generalisation of the square-gradient approximation mentioned in §2. Such a model system should be appropriate to mixtures of rare-gas liquids and, perhaps, to mixtures of other simple liquids. For parameters appropriate to Ar and Kr they find Ar segregates at the surface for bulk liquid concentrations of Ar less than O.6. Since the species with the lower surface tension is preferentially adsorbed at the surface the excess surface tension of the mixture,

$$\gamma^{ex} \equiv \gamma - x_1\gamma_1 - x_2\gamma_2 \qquad (2)$$

where x_1, x_2 are the bulk liquid concentrations and γ_1, γ_2 are the surface tensions of the pure components at the same temperature, is negative over much of the concentration range. The magnitude of γ^{ex} is, however, small $\stackrel{<}{\sim} 1$ dyn. cm.$^{-1}$ since Ar and Kr are not too different as regards their interatomic potentials. For other mixtures segregation will be more pronounced and γ^{ex} larger in magnitude. The calculations predict that for an equimolar binary mixture with equal potential well-depths, a difference in diameter of n% yields a γ^{ex} which is about n% of the difference between the surface tensions of the pure components, the larger atoms being adsorbed at the surface. For an equi-diameter mixture a difference in well-depths of m% yields a γ^{ex}

which is roughly $-m/2\%$ of the difference between the surface tensions of the pure components, the atoms with the smaller well-depth being adsorbed at the surface.

Unfortunately excess surface tensions do not appear to have been measured for mixtures of rare-gas fluids so in order to compare theory with experiment Telo da Gama and Evans [19] modelled N_2 and CH_4 using Lennard-Jones potentials and calculated γ^{ex} for $Ar - N_2$ and $Ar - CH_4$ mixtures. Given the crudeness of the potentials, the level of agreement between theory and experiment is encouraging and it seems there is now some possibility of tackling the surface properties of mixtures from a microscopic starting point.

4. Molten Salts

The thermodynamic, structural and dynamical properties of bulk molten salts have been studied intensively over the last few years (e.g. [20]). Such systems are of interest in statistical physics because their constituent particles (ions) interact via the long-ranged Coulomb force. This introduces features which are absent in those liquids where the interactions are of the short-ranged van der Waals form. The difficulties associated with the Coulomb interaction are especially relevant when we consider the surface properties of molten salts. In general there will be an electrical double layer at the liquid-vapour interface of a salt; the cations and anions will adopt slightly different density profiles in order to minimize the grand potential of the inhomogeneous fluid. Thus the molten-salt surface has many of the complications associated with electrochemical systems and any theory must make some systematic improvement on the classical Debye-Hückel or Gouy-Chapman theories of inhomogeneous charged fluids. Evans and Sluckin [21] have developed a formal density-functional theory for charged fluids and derived some explicit results for the surface properties of a model of a molten salt in which the charged particles are treated as rigid ions embedded in a structureless dielectric medium.

Calculations have not yet been performed for salts which are expected to have an electrical double layer at the surface. However, some general results concerning the magnitude of the dipole barrier have been derived [22]. In many alkali halides the cation and anion have nearly

equal radii e.g. NaF, KCl, RbCl, RbBr, CsCl and CsBr and for these salts we expect on symmetry grounds that the two density profiles are almost the same so there is only a very small double layer. Indeed for a completely 'symmetric' charged fluid where the interionic pairwise potentials are of the form

$$\phi_{\lambda\nu}(r) = \phi^{0}(r) + \frac{(-1)^{\lambda + \nu} e^{2}}{r} \qquad (3)$$

and $\phi^{0}(r)$ is the same for all species, the two profiles must be identical and the interface locally electroneutral. Under these circumstances the surface tension reduces to that of a one-component, neutral fluid and can be readily calculated. Calculations of the density profile and surface tension of the restricted primitive model, in which $\phi^{0}(r)$ is taken to be the hard-sphere potential, have been carried out over a wide range of temperature (23). Detailed results will be reported elsewhere but it appears that a simple square-gradient approximation gives a reasonable account of the measured surface tensions for the salts listed above provided the hard-sphere diameters are chosen appropriately. The theory also predicts that the interfacial thickness w for the 'symmetric' alkali-halide should be very sharp $\simeq$ 1 hard-sphere diameter near the triple point (23). A recent computer simulation (24) of the surface of liquid KCl also predicts a sharp interface i.e. somewhat sharper than those discussed in $\oint$ 2 for argon-like fluids. We are encouraged by the success of our calculations for the 'symmetric' charged fluid to extend the computations to the 'non-symmetric' alkali halides. This necessitates further approximations since theories of bulk fluids do not allow for departures from electroneutrality. Nevertheless we are confident that suitable schemes can be developed for treating the double layer etc. (22).

5.   Liquid Metals

A pure liquid metal is a two-component fluid; the ions form a dense classical liquid and the valence (conduction) electrons form a dense Fermi liquid. It is, of course, the quantum mechanical nature of the electron liquid which distinguishes the liquid metal problem from the molten salt problem and makes it more difficult! A proper theory of the liquid metal surface must be capable of describing, in a self-consistent way, a highly inhomogeneous distribution of strongly interacting ions and

electrons since we expect both the ion and electron density profiles to vary extremely rapidly at the interface. For a liquid-vapour interface there is the additional complication that somewhere in the vapour side there must be a transition from metallic-like bonding (ions plus electrons) to an insulating phase. Before reviewing various theoretical approaches it is probably worthwhile to list some questions for which theory should provide answers:

i)   What form do the density profiles adopt and what is their extent?

ii)   Which interactions determine the surface tension and its variation through the periodic table?

iii) What is the surface contribution to the work function of a liquid metal?

While i) and ii) are the same as we asked for other liquids there are important new aspects for metals. Do the electrons 'follow' the ions and vice-versa or is there a pronounced electrical double layer with the electrons extending further than the ions? In crystalline metals, where the ions are rigidly fixed in lattice planes, the electron density exhibits oscillatory behaviour in the surface layers (Friedel oscillations). Do the mobile ions in the liquid state mimic this oscillatory behaviour or are both profiles monotonic as a result of the increased thermal fluctuations? Unlike the surface tension of the liquid rare-gases which varies from 13 dyn. cm.$^{-1}$ for Ar to 19 dyn. cm.$^{-1}$ for Xe and that of the alkali-halides which lies in the range 80 - 180 dyn. cm.$^{-1}$, the surface tension of metals exhibits an enormous variation from element to element. For example, γ for Cs near its melting temperature is about 71 dyn. cm^{-1}, a value close to that of water, γ for Al is 914 dyn. cm.$^{-1}$ while γ for the high melting-point transition metal Re is about 2700 dyn. cm.$^{-1}$ (6). The temperature dependence of γ in liquid metals is also of considerable interest because of reports of positive values of $d\gamma/dT$ in some experiments (25). The quantity - $\partial\gamma/\partial T$ is the excess surface entropy per unit area and this is expected to be positive since the surface should, in some sense, be more disordered than the bulk. Indeed for almost all pure liquids, including metals, $\partial\gamma/\partial T$ is negative but for liquid Zn (25) and perhaps other metals, this coefficient is positive for temperatures up to 150 degrees above the melting point. This has been interpreted as evidence for

local ordering of atoms in the surface. Question iii) is specific to metals and, as mentioned in the introduction, concerns the magnitude of the surface dipole barrier and how this varies from the crystalline to the liquid metal.

Theoretical work prior to 1977 has been reviewed in papers by the present author (26, 27, 3) so here we will only summarize some of the main conclusions. The well-known screened-pseudoatom model which represents the potential energy of a metal as a sum of effective pairwise interionic potentials plus a volume dependent 'self-energy' contribution, and which is known to give a rather good description of the bulk properties of many simple liquid metals, appears to be inadequate for describing the interface. The surface tension can be estimated by making approximations to $\rho^{(2)}(\underline{r}_1, \underline{r}_2)$ in the interface. For the alkalis the calculated surface tensions are typically half of those which are measured while in the polyvalent metals the calculated values are typically 10-30% of the measured values (26, 27, 3). The effective pairwise potentials, as obtained from pseudopotential theory, do not have sufficiently deep minima to explain the large surface tensions of metals. This is not too surprising if we recall that most of the cohesive energy of a bulk simple metal resides in the structure independent 'self-energy' term (3). Detailed calculations of the ion density profile could, in principle, be carried out for this model using the techniques developed for monatomic liquids since the pseudoatoms form an effective one-component fluid.[+] The average electron density could then be obtained using linear response theory (3). Such computations have not been performed and, in the light of experience with the surface tension, it is doubtful whether they would yield realistic results except, perhaps, for alkali metals.

The present author (26) attempted to improve upon the linear-screening approach, which is inherent in the above model, by allowing the effective pairwise potentials and the 'self-energy' of the ion immersed in its cloud of conduction electrons to depend on the local electron density. By assuming some electron profile n(z) it was possible to calculate the ionic profile using a thermodynamic perturbation theory (27) and also the surface tension. The values of the latter were in quite good

agreement with experiment for Na, K and Al. The ionic profile was predicted to be extremely sharp; the calculated interfacial thickness w is about 1Å for Na and K and only 0.3Å for Al. These calculations were not self-consistent and no attempt was made to recalculate the electron density. Consequently it is not possible to discuss the magnitude of the dipole barrier, etc.

A somewhat more systematic way of proceeding is to follow the route introduced by Lang and Kohn (28) (see also (9)) for the surfaces of crystalline metals. This is based on the 'jellium' model of a surface in which the ions are replaced by a uniform positive background of charge with a step-function profile to represent the surface. The electron density profile and the surface energy (this is a zero temperature theory) can be calculated using the non-linear, self-consistent Hohenberg-Kohn-Sham density functional approach. The ions are re-introduced using perturbation theory, i.e. the positive charge distribution is replaced by a semi-infinite lattice of pseudo-ions giving rise to a change

$$\delta V(\underline{r}) = \sum_{\ell} v_{ps}(\underline{r} - \underline{R}_{\ell}) - V_{+}(\underline{r}) \qquad (4)$$

in the total electron-ion potential. Here $\underline{R}_{\ell}$ denotes the ionic coordinates. v_{ps} is the pseudo-potential of a single ion and $V_{+}(\underline{r})$ is the potential of the original positive background. The change in surface energy is calculated to first order in δV so that the effects of electron screening of the ions are not included. The direct ion-ion interaction gives rise to a 'classical cleavage energy'; this is just the change in Madelung energy associated with the presence of a surface. For many simple metals Lang and Kohn's calculations gave results for the surface energy which were in rather good agreement with estimates based on extrapolating measured surface tension data on liquid metals to absolute zero. (It is difficult to measure the surface tension of a crystal, so little data is available.) It is not completely obvious why this approach should work since δV can have quite large Fourier components leading to large correction terms $O(\delta V^2)$ etc. (29, 3). Recently, Monnier and Perdew (30) have improved upon the original Lang-Kohn scheme by modifying the initial jellium calculation. The perturbation introduced by the pseudoions δV is then much smaller and this should

[+] See addendum

lead to better convergence. The Lang and Kohn approach also gives a good account of the work function Φ of the simple metals. In general Φ can be written as the sum of a bulk and surface contribution:

$$\Phi = - \bar{\mu} + \Delta\phi \qquad (5)$$

where $\bar{\mu}$ is the bulk chemical potential and $\Delta\phi$, the dipole barrier, is the difference between the electrostatic potential in the vacuum and that deep inside the metal. From their calculations Lang and Kohn deduce that the magnitude of Φ is primarily determined by the jellium contribution i.e. including discrete lattice contributions via the perturbation δV changes Φ by 10% or less from its value for jellium; the change can be positive or negative depending on the particular crystal face. In the jellium calculation appropriate to a polyvalent metal such as Al, the dipole barrier $\Delta\phi$ is large since it has to cancel the large positive $\bar{\mu}$. For the alkalis $\Delta\phi$ is small and $\bar{\mu}$ is negative.

In principle it is possible to extend the Lang and Kohn approach to the liquid metal surface problem (3). By invoking the Born-Oppenheimer approximation one can construct an effective Hamiltonian for the ions interacting in the presence of the inhomogeneous electron distribution and attempt to solve the classical statistical mechanics, i.e. calculate the equilibrium ion density profile and surface tension. The difficulty arises in modelling $\rho^{(2)}(\underline{r}_1, \underline{r}_2)$ for this system of ions which interact via the bare Coulomb interaction; it is difficult to calculate the analogue of the 'classical cleavage energy'. It may, nevertheless, be possible to develop useful approximation schemes in the spirit of those mentioned in § 2. Once the ion density were evaluated the electron density could be recalculated and the process continued towards self-consistency. To our knowledge such a programme has not been carried through† so we do not have results for the profiles, dipole barrier etc. Allen and Rice (31) have performed strictly jellium calculations in which the positive background, as well as the electron distribution, is allowed to relax. They find that the ion profiles closely match the electron profiles; both profiles exhibit oscillatory behaviour for bulk electron densities corresponding to alkali metals while for higher densities the profiles

are monotonic. The interfacial thicknesses are in the range 3.5 - 6.4$\overset{\circ}{A}$. We do not find this result surprising; the minimum energy situation for a jellium of this type should correspond to local electroneutrality. Such a model gives, however, a completely unrealistic description of a real liquid metal surface. The discrete character of the ions is of crucial importance and must be taken into account. For example, Allen and Rice's calculations would presumably predict a negative work function for high density metals since $\Delta\phi$ would be almost zero. Furthermore, these calculations refer to absolute zero so there are no entropy contributions; the surface tension of a liquid metal, and certainly its temperature dependence, must be strongly influenced by the entropy associated with the configurational disorder of the ions. In a subsequent paper (32), Allen and Rice used the first order perturbation theory of Lang and Kohn to investigate discrete ion effects. They modelled the surface by close packed planes of cubic lattices and allowed the positions of the two outermost planes to relax. They argue that the Friedel oscillations in the electron density profile induce similar oscillations in the positions of the ion planes. The magnitude of the relaxation is very small, typically ~ 1% of the bulk lattice spacing. These calculations refer to absolute zero and it is not clear whether thermal motion of the ions in a liquid would enhance or reduce such effects.

As mentioned in the introduction, there is one experiment which is directly relevant to the issues raised here. Lu and Rice (8) have determined the ion density profile of the liquid-vapour interface of Hg at room temperature using a technique based on the total reflection of X-rays. They conclude that the profile is tanh-like and that the interfacial thickness is about 9$\overset{\circ}{A}$ or 3 atomic diameters. This is of the same order as that measured and predicted for argon-like fluids (see § 2) and is very much larger than the thicknesses predicted by the pseudoatom approach (27) discussed above. If the ion density profile does have a relatively large extent in Hg then

---

† See, however, S. Amokrane, J.P. Badiali, M.L. Rosinberg and J. Goodisman (these conference proceedings).

the electron profile should have an even greater extent in order to produce a significant dipole barrier. The work function of Hg does not change on melting (10) so $\Delta\phi$ should be at least 2 or 3 eV in the liquid.

It should be clear from these discussions that the theory of the liquid metal interface, even for pure simple metals, is not very satisfactory. A fresh approach is probably required. One sensible line of attack is to develop theories which treat the electrons and the ions on an equal footing. Indeed it is easy to write down a formally exact result for the surface tension and equations for the density profiles using the density functional formalism (21) mentioned in § 4 for molten salts. The derivation which leads the result (21) for the surface tension of a multi-component charged fluid does not depend on the statistics; it is valid for quantum as well as classical statistics provided the relevant coefficients are interpreted appropriately (33). These coefficients are directly related to inverses of the interacting density-density response functions of the inhomogeneous fluid, so for a liquid metal they would involve $X'_{ion-ion}$, X_{el-ion} and X_{el-el}. At present there is no feasible scheme for calculating these response functions - even the response function of the inhomogeneous electron gas at a jellium surface is not well-understood. If, however, one is willing to make a gradient expansion, as for the molten salts, it might be possible to make some headway. What is then required is a scheme for calculating the free energy density and the density-density response functions of a uniform mixture of ions and electrons for a wide range of densities. For simple metals this might be achieved using low order perturbation theory (pseudopotentials) (34). Such a theory would give a self-consistent description of both the ions and electrons and would be capable of answering, at least qualitatively, many of the questions we have posed. It would not be capable of describing Friedel oscillations if these were present. It does have the merit of being closely analogous to those theories which have been successful for classical liquids and, incidentally, to the rather successful theories of electron-hole liquid droplets in semiconductors (35).

6. Conclusions

We have deliberately focussed attention on the liquid-vapour interface of simple metals since it is for this problem that both theory and experiment might have been expected to make some progress. In contrast to other liquids, where there have been many recent developments and considerable progress, our understanding of these liquid metal surfaces remains rather poor. Satisfactory answers to the questions posed at the beginning of § 5 have not yet been provided. More experiments, as well as new theory, are necessary. Measurements of the ion density profile for other liquid metals would certainly be very useful. Is Hg a special case? It is well-known from optical reflection studies (36) on this liquid that there is a very large 'conductivity' associated with the surface. The data reported for $\partial\gamma/\partial T$ in Zn (25) remains intriguing; would careful experiments on other liquid metals yield similar behaviour? Can oscillatory ion and electron profiles produce a positive value of $\frac{\partial\gamma}{\partial T}$? Diffraction experiments on liquid surfaces have not been successful; electron diffraction has been attempted (37) but multiple scattering causes serious complications. Neutron scattering may turn out to be more useful especially when the higher intensity sources become available.

For liquid transition metal surfaces there is no theory but it should not be too difficult to develop a tight-binding theory for the surface tension along the lines suggested by Cyrot-Lackmann (38) for the surface energy of a crystalline transition metal at T = OK.

Metallurgists and physical chemists are particularly concerned with the surface tension of alloys (6, 7). There is quite a variety of behaviour observed in the concentration dependence of γ; again there is no proper theory but recently Bhatia and March (39) have proposed an interesting empirical formula which relates the concentration dependence of γ to that of the bulk liquid isothermal compressibility and to the bulk fluctuations in concentration. This appears to be a promising step towards a theory of surface segregation and γ in binary alloys. It would be interesting to see whether their formula could be put on a more rigorous theoretical foundation using the theory for mixtures mentioned in § 3. Independent measurements of the surface

concentrations of the two species would also be extremely useful.

Our current understanding of the liquid-solid interface is very primitive; even for relatively simple insulating substances statistical theories are still crude (40). For metals we have the additional complications associated with the electron distribution. It will be some time before theoretical physicists can explain why solid Fe is extremely well wetted by molten Cu but is badly wetted by molten Ag!

The author is grateful to his collaborators in Bristol, T.J. Sluckin and M.M. Telo da Gama, for many helpful discussions and permission to refer to unpublished work. He also acknowledges useful conversations with F. Flores and M. Parrinello.

References

1. M. Shimoji, 1977, 'Liquid Metals' (Academic Press: London).

2. N.W. Ashcroft and D. Stroud, 1978, Solid State Physics, 33, 1.

3. R. Evans, 1978, in 'Microscopic Structure and Dynamics of Liquids' ed. J. Dupuy and A.J. Dianoux (Nato ASI, Series B, 33: Plenum) p. 153.

4. Y. Waseda, 1977, in 'Liquid Metals 1976' ed. R. Evans and D.A. Greenwood (Inst. Phys. Conf. Series No. 30) p. 230.

5. A. Meyer, M.J. Stott and W.H. Young, 1976, Phil. Mag., 33, 381.

6. B.C. Allen, 1972, in 'Liquid Metals Chemistry and Physics' ed. S.Z. Beer (Dekker: New York) p. 161.

7. V.K. Semenchenko, 1961, 'Surface Phenomena in Metals and Alloys' (Pergamon: Oxford).

8. B.C. Lu and S.A. Rice, 1978, J. Chem. Phys., 68, 5558.

9. N.D. Lang, 1973, Solid State Physics, 28, 224.

10. C. Norris, 1977, in 'Liquid Metals 1976' ed. R. Evans and D.A. Greenwood (Inst. Phys. Conf. Series No. 30) p. 171.

11. J. Hölzl and F.K. Schulte, 1979, Springer Tracts in Mod. Phys., 85, 1.

12. R. Evans, 1979, Adv. in Phys., 28, 143.

13. F.F. Abraham, 1979, Phys. Rep., 53, 93.

14. S. Toxvaerd, 1975, in 'Statistical Mechanics' Vol. 2, ed. K. Singer (The Chemical Society) p. 256.

15. D. Beaglehole, 1979, Phys. Rev. Lett., 43, 2016.

16. J.D. van der Waals, 1894, Z. Phys. Chem., 13, 657. This classic paper has been translated into English - J.S. Rowlinson, 1979, J. Stat. Phys., 20, 197.

17. M.M. Telo da Gama and R. Evans, 1979, Mol. Phys., 38, 367.

18. M.H. Kalos, J.K. Percus and M. Rao, 1977, J. Stat. Phys., 17, 111.

19. M.M. Telo da Gama and R. Evans, 1980, Mol. Phys. (to appear).

20. M. Parrinello and M.P. Tosi, 1979, Riv. del. Nuovo Cimento, 2, 1.

21. R. Evans and T.J. Sluckin, 1980, Mol. Phys. (to appear).

22. T.J. Sluckin (to be published).

23. M.M. Telo da Gama and R. Evans (to be published).

24. D.M. Heyes and J.H.R. Clarke, 1979, J.C.S. Faraday II, 75, 1240.

25. D.W.G. White, 1966, Trans. Metall. Soc. AIME, 236, 796.

26. R. Evans, 1974, J. Phys. C., 7, 2808.

27. R. Evans and R. Kumaravadivel, 1976, J. Phys. C., 9, 1891.

28. N.D. Lang and W. Kohn, 1970, Phys. Rev. B, 1, 4555. Ibid., 1971, Phys. Rev. B, 3, 1215.

29. M.W. Finnis, 1975, J. Phys. F., 5, 2227.

30. R. Monnier and J.P. Perdew, 1978, Phys. Rev. B, 17, 2595.

31. J.W. Allen and S.A. Rice, 1977, J. Chem. Phys., 67, 5105.

32. J.W. Allen and S.A. Rice, 1978, J. Chem. Phys., 68, 5053.

33. R. Evans and T.J. Sluckin, 1980, J. Phys. C., 13, L77.

34. J. Chihara, 1976, Prog. Theor. Phys., 55, 340. S.A. Trigger, 1976, Phys. Lett., 56A, 325. S. Cusack, N.H. March, M. Parrinello and M.P. Tosi, 1976, J. Phys. F., 6, 749.

35. T.M. Rice, 1977, Solid State Physics, 32, 1.

36. A.N. Bloch and S.A. Rice, 1969, Phys. Rev., 185, 933.

37. R.M. Goodman and G.A. Somorjai, 1970, J. Chem. Phys., 52, 6331.

38. F. Cyrot-Lackmann, 1968, J. Chem. Phys. Sol., 29, 1235.

39. A.B. Bhatia and N.H. March, 1978, J. Chem. Phys., 68, 4651.

40. G. Navascues, 1979, Rep. Prog. Phys., 42, 1131.

Addendum

Since the completion of this article we have learnt that K.K. Mon and D. Stroud (to be published) have calculated the ion density profile and the surface tension using the pseudoatom model. These authors use a square-gradient approximation of the type described in $\S$2; the direct correlation function which enters such an approach is calculated using a pairwise interionic potential corresponding to half the bulk liquid density. At this reduced density the pairwise potential is quite deep and Mon and Stroud calculate surface tensions which are in rather good agreement with experiment for a wide range of simple liquid metals. They also estimate an interfacial thickness which is in reasonable agreement with the experimental result for Hg(8).