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THERMODYNAMICS.

THERMODYNAMIC ASPECTS OF LIQUID AND AMORPHOUS METALS

M. Shimoji

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan.

Abstract.- The present understanding of thermodynamic properties of liquid and amorphous metals is outlined. The problem of inter-atomic forces in metals is also briefly described.

1. INTRODUCTION

It is now known that the thermodynamics of simple (or NFE: nearly free electron) liquid metals is understandable microscopically in terms of both the pseudopotential theory and the liquid state theory, as was reviewed by Young [1] in the Bristol conference. This approach becomes increasingly strengthened by refining the details of calculations. It starts from the fact that the total potential energy of a metal with N atoms can be written [2-4]

$$U(\vec{R}_1, \dots, \vec{R}_N) = U_g + \frac{1}{2} \sum_{i \neq j} u(|\vec{R}_i - \vec{R}_j|), \quad (1)$$

where \vec{R}_i is the ionic coordinate; U_g the potential energy which depends only on the ionic (number) density of the metal, n , and not on the ionic arrangement; $u(R)$ the effective pairwise potential between the ions. Within the usual framework of pseudopotential theory the interionic pair potential $u_{ps}(R)$ comes from the direct point charge interaction and the polarization effect of the electron gas to be represented by the electron dielectric function which is also density-dependent.

For the ions with large core radii the exchange repulsive energy term, $u_{rp}(R)$,

caused by core electrons should also be taken into account, e.g. using the equation of the Born-Mayer type. Moreover, for highly-polarizable ions the dispersion or van der Waals forces due to instantaneous dipole-dipole interactions, $u_{vW}(R)$, are not always negligible, even though the ions are immersed in the electron gas [5-7]. Thus, an accurate expression for $u(R)$ in (1) should be given by

$$u(R) = u_{ps}(R) + u_{rp}(R) + u_{vW}(R). \quad (2)$$

At normal densities of simple metals both u_{rp} and u_{vW} are small enough to be ignored, but not always for non-simple metals [5,7].

The binding energy of a metal is determined largely by the structure-independent energy U_g in (1) [2,8], which is a sum of the well-known electron gas energy U_{eg} in the uniform positive background and the electrostatic energy U_{ei} of the electron gas with pseudopotentials embedded with it. The U_{ei} is strongly influenced by the pseudopotential used, since it contains the first-order perturbation term.

For transition metals the renormalized-atom method is now being developed to describe the binding properties [9].

From the point of view of the tight binding method Friedel [10] proposed another model for the binding of transition metals formed by overlapping of the d-orbitals of the free atoms. It would be still reasonable to expect the existence of the strongly structure-dependent pair potential $u(R)$ for such liquid transition metals, whose form is analogous to that in (1); for example, the one component plasma model [11] is a simple approach for this problem.

Once the potential energy U of a liquid metal is given as in (1), the microscopic calculation of its thermodynamic properties can be made straightforwardly by employing the technique of the statistical mechanical theory of classical molecular liquids. A slightly modified calculation can also be made for the amorphous state.

2. CRUDE MODEL FOR LIQUID METALS

The simplest model of a liquid metal is obtained by expressing $u(R)$ in (1) by a hard sphere model which is characterized by the diameter σ or the packing fraction $\xi = \pi\sigma^3 n/6$. Analytical equations of state for the hard-sphere fluid are given in the form of Percus-Yevick [12] or Carnahan-Starling [13] equations, which are in good agreement with computer-simulation studies at packing densities with ξ smaller than ~ 0.5 ; in consequence, the hard-sphere Helmholtz free energy F_{hs} can readily be derived. Thus, the total Helmholtz free energy of a liquid metal is given by [2]

$$F = U_g + F_{hs} \quad (3')$$

from which other thermodynamic quantities can easily be calculated. For example, the entropy $(= -(\partial F/\partial T)_V)$ may be written in the sum of the electronic part S_{elec} and the hard-sphere part S_{hs} [1]. Usually S_{elec} is small enough to be neglected because of highly degenerate nature of the electron gas except for liquid transition metals [1,17,18], and S_{hs} has been calculated by using the value of ξ fitted to the diffraction data or that derived from thermodynamic perturbation calculations (Section 3); calculated entropy results are quite reasonable [1-4, 14-16]. A different type of discussion for the entropy has also been proposed [19] by modifying the earlier phonon theory [20].

The thermodynamic data of expanded liquid metals have been discussed from the same point of view as for equation (3) [21, 22]. For Hg marked changes in quantities corresponding to $\partial U_g/\partial v$ were observed [22] in the metal-semiconductor transition region.

3. AB INITIO CALCULATIONS

First principles calculations of the thermodynamic properties of NFE liquid metals and alloys have been made mostly by applying the thermodynamic perturbation theory to a system whose effective potential energy is given in the form of (1). This approach [1-14] is based on the Gibbs-Bogolieubov inequality and the reference system chosen is the hard sphere fluid whose model parameter σ (or ξ) is usually determined with the use of variation principles. But the pseudopotentials used in

these calculations are still not accurate enough to allow a precise comparison of calculated thermodynamic quantities with experiment. For example, Hafner [23] showed that, even if a carefully optimized OPW pseudopotential was used, some additional parameter was necessary to obtain the correct zero-pressure density for pure liquid metals. The use of such adjusted pseudopotentials (for the pure state) leads to semiquantitative agreements for the excess quantities of NFE liquid alloys on mixing [23,24] (see tables 1 and 2). Similar but non-perturbative calculations [2,25] were also made, most of which were somewhat semi-empirical because of the use of experimental structure factors. The phase diagram of alloys can be calculated using the pseudopotential theory [26].

4. STABILITY AND CHARGE TRANSFER IN LIQUID ALLOYS

The condition of thermodynamic stability for a binary alloy at constant temperature T and pressure p is known to be given by $\partial^2 G / \partial x_\alpha^2 > 0$, where G is the Gibbs free energy and x_α the atomic fraction of the species α . This important quantity is inversely proportional to the long wavelength limit of the concentration fluctuation structure factor $S_{CC}(q)$ introduced by Bhatia and Thornton [27]:

$$S_{CC}(0) = Nk_B T / (\partial^2 G / \partial x_\alpha^2)_{T,P,N} \quad (4)$$

Thus, to know $S_{CC}(0)$ of a liquid alloy is to know its stability [28]. Extensive studies on $S_{CC}(0)$ of many alloy systems have been made [29]; significant devi-

Table 1. Volume, enthalpy and entropy of mixing for equiatomic binary alloys [23]. Experimental values are given in parentheses. Theoretical values of $\Delta v/v$ due to [24] for NaK and AlMg are nearly the same as experimental results. Units for ΔH^M and ΔS^M are cal/g·atom and cal/g·atom K.

Alloy	T(°C)	$\Delta v/v(\%)$	ΔH^M	ΔS^M
NaK	100	-1.8 (-1.4)	470 (174)	1.03 (1.35)
NaCs	100	-7.1 (-5.4)	1870 (218)	0.33 (1.20)
AlMg	665	-4.3 (-3.0)	-1980 (-806)	1.19 (1.18)

Table 2. Isothermal bulk modulus B_T and thermal expansion coefficient α_p for equiatomic NaK alloy (373 K) [23], [24]† Experimental values are given in parentheses.

B_T (10^{10} dyn cm $^{-2}$)	α_p (10^{-4} K $^{-1}$)
2.6, 3.65† (3.3)	5.1, 2.99† (2.7)

ations from ideality are found for metal-nonmetal mixtures such as Cs-CsCl [30].

In spite of considerable difficulties involved in small-angle scattering experiments, some encouraging results have been reported to verify directly the equivalence of both sides of equation (4); e.g. Li-Pb [31], Cu-Sn [32], Na-Ga [33], Cu-Bi [34], Na-Cs [35], Sb-Zn [36], Tl-Te [37]. But the situation is different in the data reported by Desre and co-workers [38] for liquid Ag-Ge alloys, scattering results of which were too large to be interpreted in terms of equation (4) (table 3); then the presence of long heteroatomic chains was proposed. We note that equation (4) was derived under the condition that fluctuations are so small that deviations from the most probable concentration can be described without error using the Gaussian

probability distribution. A more careful analysis appears to be required in such cases, as well as in critical or two-phase solutions.

Another parameter has also been introduced [39] to describe the departure from the mean composition in liquid alloys.

The problem of charge transfer is of central importance in the understanding of the alloy thermodynamics [2]. In principle, this problem can be discussed from the pseudopotential [21], tight-binding method [40-42] and other approaches [43]. More speculatively, various kinds of scales for elements have been proposed to show the tendency of charge transfer in alloys [44-48]. Most of such discussions have been developed without obvious distinction between liquid and solid phases. We note that in some such recent proposals the angular momentum dependence of charge-transfer parameters has been emphasized, the effect of which can be observed experimentally; e.g. for soft X-ray [49] and photoemission [50] studies. The effect of charge transfer plays an important role in the problem of metal-nonmetal transitions in "semiconducting" alloys (e.g. Tl-Te) and "ionic alloys (e.g. Cs-Au) [2, 51-53].

5. THERMAL BEHAVIOUR OF METALLIC GLASSES

Rapid quenching of liquid alloys leads to the formation of amorphous alloys (or metallic glasses), in which the long-range periodicity of atomic arrangement is lost. In this process melts are cooled to temperatures well below their melting points, T_m , without crystallization. The transition of

Table 3. Comparison of experimental and theoretical differential coherent scattering cross section (10^3 cm^{-1}) at the limit of $q=0$ for Ag-Ge alloys [38]. * : the absolute uncertainty in experimental values.

x_{Ag}	T(K)	exp.	theor.
0.86	1101	5.63 (1.40*)	0.51
0.60	1101	1.88 (0.47*)	0.54
0.402	1103	2.53 (0.63*)	0.75

such supercooled liquids to the glassy state is caused by the slowness of atomic motion below a certain temperature called the glass transition temperature T_g .

Usually the glass transition is associated with no sudden changes in the enthalpy H and the volume V but abrupt changes in the heat capacity C_p and the thermal expansion coefficient α_p . Thus, it has a characteristics of second-order transition [54-56]; see Fig. 1. We note that T_g is

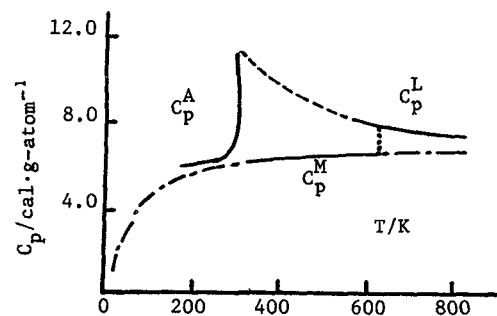


Fig. 1. Heat capacity of $\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.094}$ alloy, taken schematically from [55]. L: liquid, A: amorphous, M: ideal solid mixture; — exp., ---- extrapolated, -.-.- ideal mixture. m.p : 625 K.

not a constant of the material since it is a function of experimental conditions imposed; the ideal T_g would be the one at which the transition occurs upon infinitely slow cooling [57]. The value of T_g is thus 'diffuse', so that the glass transition

should be described as a 'diffuse' second-order thermodynamic transition [58].

Most metallic glasses produced to date are those obtained by cooling metallic alloys (near eutectic compositions); pure liquid metals have not in practice been quenched into a glassy state. For glass forming alloys Chen and Jackson [59] emphasized two common features: considerable interaction between unlike constituent atoms as represented by a negative heat of mixing and relatively low melting temperatures (deep eutectic points). Chen also [60] proposed that the glass forming stability of amorphous alloys is determined largely by the destabilization of the crystalline mixture rather than the stabilization of the glassy state near the eutectic composition. Thermodynamic measurements are important to reveal the relative stability of such phases [55,61,62].

6. MODEL APPROACHES TO THE AMORPHOUS STATE

According to diffraction studies on amorphous metals [63], their structure is similar to that of metallic liquids. The experimental radial distribution function of many metallic glasses are known to be described successfully in terms of the model of dense random packing of hard spheres (DRPHS). The packing fraction ξ in this model is, however, about 0.64 for amorphous metals [64], which is much larger [65] than the values, about 0.46, in hard sphere model description of liquid metals at the melting points [2,14]

From a molecular dynamics computation for the hard-sphere fluid at various

densities Woodcock [58] found that the amorphous close-packed density is given by $n_a \sigma^3 = 1.217$ (corresponding to $\xi = 0.637$), and that the glass transition is of a 'diffuse' thermodynamic transition of third-order. In real systems with soft attractive potentials the glass transition is, however, the 'diffuse' second-order, as described above, because there is a non-vanishing contribution to second-order properties from potential energy fluctuations. In an improved model more realistic pair potentials between the atoms should be considered; an example is the relaxed model [66] (see also [67]).

The entropy theory of glass transition was developed by Adam and Gibbs [68], by which the size of a cooperatively rearranging region in a glass-forming liquid can be estimated. This theory permits us to evaluate the equilibrium second-order transition temperature T_2 (or ideal T_g) where the configurational entropy should vanish. The study of such equilibrium glass transitions is important to accentuate the features of relaxation phenomena. Cohen and Grest [69] discussed this problem by proposing a percolation theory of the free volume model, in which the existence of solid-like and liquid-like cells was assumed.

In view of the structural resemblance to liquid metals, thermodynamic properties of amorphous metals can be discussed using theoretical methods similar to those developed for liquid metals and alloys. In fact Hafner and von Heinmendahl [70] (see also [11]) first attempted to apply the

pseudopotential approach (described in Section 3) to transition-metal-free glasses (Mg-Zn, Ca-Mg and Ca-Al), and found that the glassy and liquid state are stabilized by the close matching of the minima in $u(R)$ and the maxima in the pair correlation functions; this may be related to the Nagel-Tauc criterion [72] for the glass-forming ability. The average packing fraction derived in this way for the Mg₇Zn₃ alloy at 25°C was 0.62, close to the value in the DRPHS model; the Percus-Yevick hard-sphere structure factors derived resembled those due to the relaxed model; calculated excess thermodynamic functions of the Ca-Mg amorphous alloy were very similar to the corresponding result for the liquid alloy.

Such microscopic calculations of thermodynamic properties as well as those of relaxation behaviour [73] are important to know fundamentally how glass transition takes place in the supercooled-liquid and glassy states of metals.

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