



## A SIMPLE SCALING FORMULA AND MONTE CARLO STUDY OF LIQUID SEMICONDUCTOR SURFACES: APPLICATION TO $Cd_xTe_{1-x}$

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(Received June 27, 1994)

(Revised August 10, 1994)

### 1. Introduction

Many physical processes are strongly influenced by surface tension. For example, crystal growth of semiconductor compounds in a microgravity environment depends on the temperature- and concentration derivatives of surface tension. In such situations, gravity-driven convective forces are suppressed, and the dominant one is the so-called Marangoni convection, which is driven by surface tension gradients parallel to the surface. A particularly interesting material from this point of view is liquid  $Cd_xTe_{1-x}$ . In its solid phase, only a single stoichiometric compound exists, and this is nearly insoluble in either pure Cd or pure Te. The liquid phase forms a continuous solid solution at all temperatures above the liquidus. The stoichiometric compound is semiconducting, with a very low electrical conductivity of  $\approx 90 \Omega^{-1}cm^{-1}$  at the melting temperature. The conductivity rises sharply on either side of the stoichiometric composition, suggesting that the semiconducting liquid is rapidly transformed by the addition of electrons or holes to a quasi-metallic electronic structure as it departs from stoichiometry. The viscosity also shows anomalous behavior near the 50-50 liquid[1].

In previous papers[2,3], we have treated the surface properties of liquid Si and stoichiometric liquid CdTe by a Monte Carlo technique, using empirical two and three-body potentials of the type first proposed by Stillinger and Weber. Although these potentials are purely empirical, they agree well with experiment. For example, they predict elastic constants, heats of fusion, and surface tensions in good agreement with experimental data. The extension of this work to nonstoichiometric CdTe would seem to be complicated by the anomalous transport data mentioned above. This data suggests that, as one leaves stoichiometry by 10 at. % or more, electrons or holes are excited which rapidly screen whatever interatomic potentials are operating in the stoichiometric state. Thus, one would expect to need to change those potentials in order to get believable results far from stoichiometry.

As a first step in understanding nonstoichiometric  $Cd_xTe_{1-x}$ , we describe in this paper Monte Carlo calculations for such alloys using the *same* potentials as used for  $x = 0.50$ . These lead to the apparently anomalous prediction that the surface tension of  $Cd_xTe_{1-x}$  is a nonmonotonic function of  $x$ . While there are no available experimental results for  $Cd_xTe_{1-x}$  with determined  $x$  except at  $x = 0.5$ , other semiconductor alloys do exhibit such an anomaly, which is therefore evidently accounted for by our empirical potentials.

In order to shed more light on this anomaly, we also analyze it by means of a scaling formula for the surface tension, which we have briefly introduced in a previous paper[3]. This scaling formula permits us to calculate the surface tension from only two parameters in the potentials. Here, we apply this scaling formula to other elemental and compound liquid semiconductors as well as to off-stoichiometric CdTe. The scaling results are in good agreement with the Monte Carlo results and available experiments.

We use empirical potentials only because the true electronic structure of the liquid is so complex that a microscopic treatment is not yet feasible. In principle, it would be desirable to treat electronic and ionic degrees of freedom on the same basis by use of a technique such as that introduced by Car and Parrinello for liquid Si[4]. But at present, the application of these techniques to materials with a free surface would probably require a prohibitive amount of computer time. The use of empirical potentials allows treatment of a range of alloys with far less computer time.

The remainder of this paper is organized as follows. Section II describes our Monte Carlo method. The scaling formula is described and extended in Section III. Results are presented and discussed in Section IV.

## 2. Method and Formalism

To calculate the bulk thermodynamic properties of nonstoichiometric  $Cd_xTe_{1-x}$ , we apply standard Monte Carlo techniques to a supercell containing  $6 \times 6 \times 6 = 216$  atoms with periodic boundary conditions. The surface properties are calculated using a direct evaluation of the surface free energy as proposed by Miyazaki, Barker, and Pound[5]. The interatomic potentials are chosen to be the same as those used previously for stoichiometric CdTe. They are a combination of two- and three-body potentials of the Stillinger-Weber type[6], with parameters chosen to fit the bulk atomization energy, nearest neighbor separation, and melting temperature. The details of these potentials, and of the method used to obtain the parameters, have been given in previous papers[2,3]. Our calculations using these potentials are valid, at best, only close to the stoichiometric composition, since only there can the atoms be reasonably assumed to lie in an approximately tetrahedral arrangement as is implicitly assumed in fitting our potentials. At larger deviations, the potentials will be strongly affected by the screening produced by charge carriers excited above the gap.

To calculate the surface tension at different temperatures, we adopt a very efficient technique presented in our previous paper[7], which is an extension of an approach of Ferrenberg and Swendsen[8], whereby complete thermodynamic information can be obtained over a broad temperature or Hamiltonian parameter region using only one or few Monte Carlo simulations. This strategy is very useful in calculating the parameter dependence of various thermodynamic quantities over a limited parameter range. It is ideally suited to calculating temperature derivatives, since these require a temperature range which is as small as possible.

Scaling relations connecting the surface tension and various bulk properties have been frequently proposed[9,10]. Similar scaling relations have been developed to describe the cohesion, adhesion, and chemisorption of molecules[11]. These relations are characterized as universal in the sense that they apply to large groups of pure elements. But among these elements, the tetrahedral semiconductors are often least accurately described, presumably because of their non-closed-packed structure. In our previous work[3], we deduced a different scaling theory based on the results of Monte Carlo simulations for liquid CdTe and Si. Here we present the scaling relation in a more systematic way, and subject it to a more wide-ranging test than previously.

Our scaling relation can be written as

$$\tau(T) = \alpha(k_B T / \epsilon) \frac{\epsilon}{\sigma^2} \quad (1)$$

where  $\epsilon$  and  $\sigma$  are two of the parameters entering the empirical potentials:  $\epsilon$  is the bond energy, and  $\sigma$  is defined so that the nearest neighbor separation in the solid phase is  $2^{1/6}\sigma$ . These parameters are, of course, proportional to the binding energy and lattice constant of the solid phase. The dimensionless variable  $\alpha$  is assumed to be a universal function of the reduced temperature  $T^* = k_B T / \epsilon$ , where  $T$  is the absolute temperature. Over a limited temperature range, we approximate  $\alpha$  as a linear function of the reduced temperature  $T^*$ :

$$\alpha = 0.112 - 0.636(T^* - 0.07) \quad (2)$$

which fits our previous Monte Carlo results for Si and stoichiometric CdTe. Hence, in this linear approximation, the temperature derivative of the surface tension takes the form

$$\frac{d\tau}{dT} = -0.636 \frac{k_B}{\sigma^2} \quad (3)$$

Thus, in this linear approximation to the scaling function,  $d\tau/dT$  is independent of temperature, and depends only on the lattice parameter of the alloy, not on the bond strength parameter  $\epsilon$ .

Although this scaling relation was originally inferred from Monte Carlo calculations for Si and stoichiometric CdTe, a comparison of the relation with all available experimental values of the surface tension of both elemental and compound tetrahedral semiconductors at their melting temperature is encouraging. Fig. 1 shows the reduced surface tension of these materials as the function of their reduced melting temperature  $T_m^*$ . To compute  $\alpha$  and  $T_m^*$ , the values of the bond-strength parameter  $\epsilon$  and the bond-length parameter  $\sigma$  are inferred from the binding energies  $E_b$  and nearest-neighbor distances  $a$  quoted in Ref. [12], using the relations  $\epsilon = \frac{1}{2}E_b$ ;  $\sigma = 2^{-1/6}a$ . We find that all the experimental results fall near but slightly below the straight line described by eq. (2). In view of the uncertainties inherent in both the Monte Carlo calculation and the experimental measurement (which, for example, vary among themselves by more than 15 % for elemental Si near the melting point[13]), this is still good agreement between the scaling theory and measured results.

To extend the scaling relation to a compound semiconductor (say  $A_xB_{1-x}$ ) off stoichiometry, we assume that the interactions are independent of concentration. As discussed earlier, this assumption will be adequate at best only near stoichiometry. We also assume that all the bonds at stoichiometry are between *unlike* neighbors. As the concentration of one component (say A) is increased, we assume that the B atoms in the bonds are randomly replaced by A, in such a way that both A and B still have their proper global concentrations. Thus the parameters  $\epsilon$  and  $\sigma$  appearing in the scaling formulas are to be replaced by *effective parameters*  $\bar{\epsilon}$  and  $\bar{\sigma}$  given by simple arithmetic averages:

$$\bar{\epsilon}(\Delta x_A) = \epsilon + 2\Delta x_A(\epsilon_{AA} - \epsilon) \quad (4)$$

$$\bar{\sigma}^3(\Delta x_A) = \sigma^3 + 2\Delta x_A(\sigma_{AA}^3 - \sigma^3), \quad (5)$$

where  $\Delta x_A = x_A - 0.5$ ,  $x_A$  being the atomic concentration of the majority element. The parameters  $\epsilon_{AA}$  and  $\sigma_{AA}$  are fitted to the atomization energy and nearest neighbor separation of pure element A arranged in a fictitious diamond structure, as discussed in Ref. 3. Their values are, in the sequence of Cd-Te, Cd-Cd, Te-Te, 1.03, 0.58, 1.115 eV/atom for  $\epsilon$ , and 0.2508, 0.2659, 0.2552 nm for  $\sigma$ . The parameter  $\epsilon$  refers to the potential between unlike elements (A and B), and is the only potential that need to be considered in the stoichiometric alloy.

Using eqs.(1), (2), (4) and (5), we obtain, to first order in  $\Delta T^*$  and  $\Delta x_A$ ,

$$\frac{\tau(\Delta x_A, \Delta T^*)}{\tau(0)} = 1 + \Delta x_A \left[ -7.571 \frac{\Delta T^*}{\Delta x_A} - 3.726 \left( 1 - \frac{\epsilon_{AA}}{\epsilon} \right) + \frac{4}{3} \left( 1 - \frac{\sigma_{AA}^3}{\sigma^3} \right) \right]. \quad (6)$$

where  $\Delta T^* = k_B(T - T_m)/\epsilon$  and  $T_m$  is the melting temperature of the stoichiometric alloy. Given the values of  $\epsilon$  and  $\sigma$  for the excess constituent, eq. (6) can be used to give the surface tension of the alloy off stoichiometry.

### 3. Results and Discussion

In Table 1, we list the surface tension as calculated from the scaling formula (6) at 45 % and 55 % Cd. The surface tensions are listed along two curves: the isotherm corresponding to the melting temperature of stoichiometric CdTe; and the liquidus curve. (The liquidus is taken from Ref. 14.) As is clear from the table, the effect of temperature changes is comparable to that of changes in concentration. In both cases, however, although elemental Cd has a higher surface tension than CdTe, an excess of Cd actually reduces the surface tension. Similarly, a slight excess of low-surface-tension Te is predicted actually to increase the surface tension. Of course, this behavior is predicted only for a small excess concentration, since our assumptions about the interactions between like atoms are unphysical when there is a large excess of one species. In that case, the interaction between atoms of the excess species should be similar to that in the pure element, rather than to the potential in the fictitious diamond structure as assumed in the scaling model. Therefore, as the concentration is off stoichiometry further, it is expected that the surface tension will start to increase as excess Cd increases, and decrease as excess Te increases, as measured in the work reported in Ref. 17. Unfortunately, the inability in Ref. 17 to determine the excess concentration and the large standard deviation prevent us from confirming our prediction

for the surface tension behavior in very small excess concentrations. To our surprise, the seemingly counter-intuitive prediction of Table 1 has been confirmed in experiments carried out in other compound semiconductors. Fig. 2 shows the surface tension of molten GaSb and InSb, as measured by Dasherskii *et al*[15]. Although the surface tension decreases monotonically over most of the concentration range, there is clearly a reverse behavior around the stoichiometric composition, as in our calculations. However, the reversal is confined to a smaller concentration range than where our calculation is carried out. This is presumably due to the fact that the potentials in the real alloy are strongly screened as one departs from stoichiometry. The prediction in Table 1 should be only valid within smaller excess concentration range.

Table 2 shows the Monte Carlo predictions for the surface tensions, bulk specific heat, and temperature derivative of the surface tension at two concentrations slightly off stoichiometry. All calculations were carried out at a temperature slightly above the melting temperature of the stoichiometric alloy. The specific heat is calculated both from the fluctuation expression [ $C_V = (\langle E^2 \rangle - \langle E \rangle^2)/k_B T^2$ ], and from the temperature derivative [ $C_V = d \langle E \rangle / dT$ ], where  $E$  is the energy and  $\langle \dots \rangle$  denotes an average in the canonical ensemble, and the temperature derivative is obtained by the method of Ferrenberg and Swendsen[7,8]. Both results are equal to within numerical accuracy. The temperature derivative of the surface tension is also obtained by two methods. The first involves calculating the negative of the surface entropy, and using the relations  $(d\tau/dT)_{ent} = -S_s = (\tau - E_s)/T$ , where  $S_s$  and  $E_s$  are the surface entropy and surface energy per unit area. The other method is that of Ref. 7 and 8, as described above. The consistency of the two methods is remarkable: both derivatives agree to two decimal places at all three concentrations considered.

TABLE 1.

Scaling results for the  $Cd_xTe_{1-x}$  system at the melting temperature.  $T_m$  is the melting temperature,  $\tau(T = 1090^\circ C)$  is the surface tension (in N/m) at the melting temperature of the stoichiometric alloy, and  $\tau(T = T_m)$  is the surface tension (in N/m) along the liquidus;  $d\tau/dT$  is calculated in  $N/m^\circ C$ .

Cd%	55%	50%	45%
$T_m(^{\circ}C)$	1040	1090	1120
$\tau(T = 1090^{\circ}C)$	0.197	0.218	0.221
$\tau(T = T_m)$	0.204	0.218	0.225
$d\tau/dT$	$-1.4 \times 10^{-4}$	$-1.4 \times 10^{-4}$	$-1.4 \times 10^{-4}$

TABLE 2.

Monte Carlo results for  $Cd_xTe_{1-x}$  at  $T=0.12$  ( $1160^\circ C$ ). The columns denote atomic percent Cd; specific heat (in  $k_B/atom$ ); and surface tension (in N/m); temperature derivative of surface tension (in  $N/m^\circ C$ ).

Cd%	54%	50%	45%
$C_V(\pm.2)$	3.3	3.3	3.4
$\tau$	0.191	0.213	0.223
$(d\tau/dT)$	$-1.5 \times 10^{-4}$	$-0.9 \times 10^{-4}$	$-1.0 \times 10^{-4}$

The results of the Monte Carlo simulations are plotted in Fig. 3, together with our scaling results and the experimental data. Evidently the Monte Carlo calculations are consistent with the scaling predictions. In particular, both approaches predict a nonmonotonic variation of surface tension with composition near stoichiometry. The calculated surface tension is nonmonotonic over a wider range of concentration than is observed in other compound semiconductors [cf. Fig. 2], probably because we use concentration-independent potentials in our calculations. In particular, the Monte Carlo calculations at 45 % Cd are probably carried out too far from stoichiometry for the potentials to be valid.

Fig. 4 shows the density profiles obtained from our Monte Carlo simulations at 45 % concentration of Cd. We believe that the various bulk oscillations are simply artifacts of imperfect statistics. They would probably disappear if the Monte Carlo runs were continued for a longer time, or were carried out for larger samples. As in the stoichiometric case previously reported, there is a clear trend for Cd to migrate to the surface. Note also that, for the rather small supercell used in these calculations, the existence of excess Cd on the surface produces a spurious decrease of Cd concentration in the bulk of the sample. This is a finite size effect, and would be reduced if the supercell were enlarged for greater accuracy.

To conclude, we have described in detail a scaling formula for calculating the surface tensions of liquid semiconductors and their alloys. We have shown that this scaling formula describes with reasonable accuracy a number of such semiconductors, including liquid CdTe both on and off stoichiometry. The scaling predictions are confirmed by Monte Carlo calculations applied to an alloy described by empirical potentials. In particular, both the scaling theory and the Monte Carlo calculations predict that the surface tension of  $\text{Cd}_x\text{Te}_{1-x}$  has a nonmonotonic variation with composition, such as is observed experimentally in other semiconductor alloys.

#### Acknowledgements

We are grateful to Dr. Alan J. Markworth and Dr. M. D. Lind for sending us references and for helpful discussions. This work has been supported by the U. S. National Aeronautics and Space Administration through Grant No. NAG3-1437. Calculations were carried out using a grant of time from Ohio Supercomputer Center.

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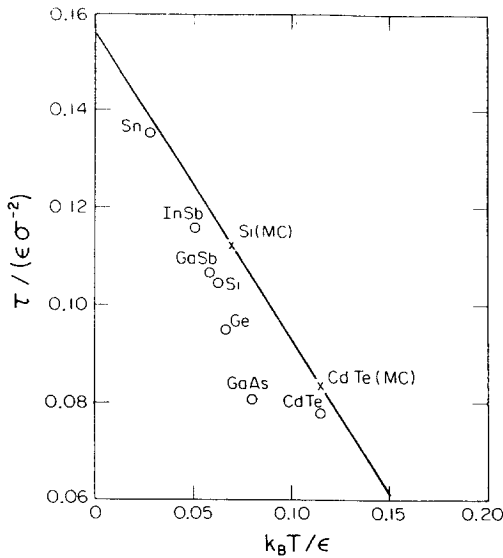


FIG. 1. Reduced surface tension  $\alpha = \tau/\epsilon\sigma^2$  plotted as a function of reduced melting temperature  $T^* = k_B T_m/\epsilon$ . Open circles: experimental surface tensions as taken from Refs. 9, 15, 16, and 17, Crosses: Monte Carlo surface tensions, from Refs. 2 and 3. The straight line has the equation  $\tau/(\epsilon\sigma^2) = 0.112 - 0.636(T^* - 0.07)$ .

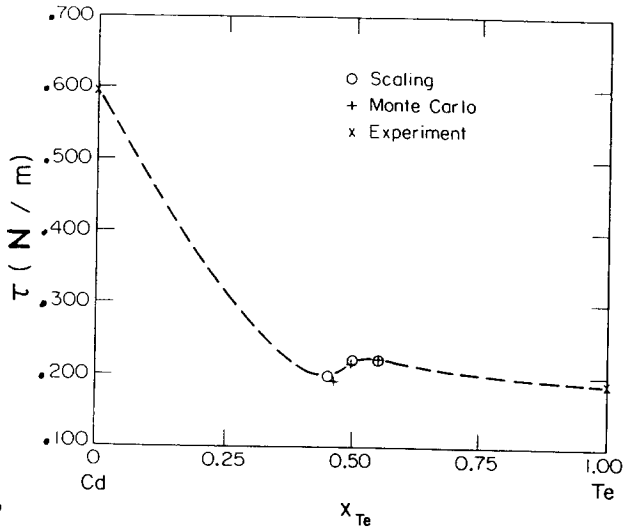


FIG. 3 The surface tension of liquid  $Cd_x Te_{1-x}$ . The symbol 'x' denotes the experimental data at the melting temperature (see Ref.9); 'o' indicates the prediction of our scaling formula at temperature 1090 °C; and '+' represents our Monte Carlo results at temperature 1160 °C. The dashed line is only a guide to the eyes.

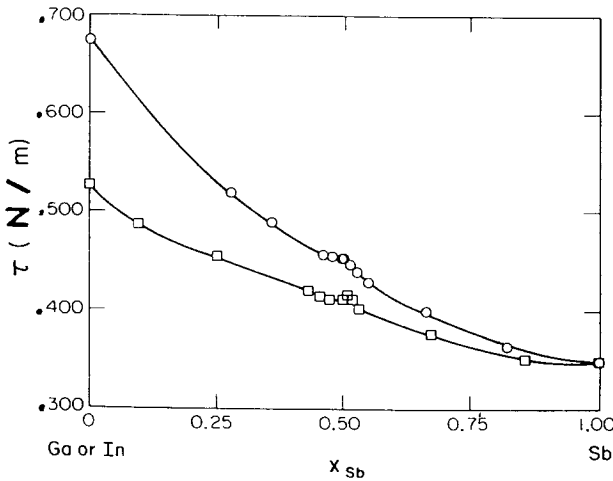


FIG. 2. Measured surface tensions of liquid  $Ga_x Sb_{1-x}$  and  $In_x Sb_{1-x}$ , as quoted in Ref. 15. The upper curve refers to  $Ga_x Sb_{1-x}$  at temperature 725°C. The lower curve, to  $In_x Sb_{1-x}$  at temperature 550°C.

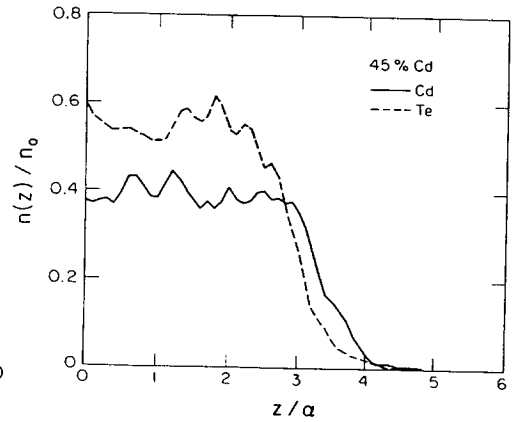


FIG. 4. Partial density profiles for a liquid  $Cd_{0.45} Te_{0.55}$  surface at a reduced temperature  $T^* = 0.12$  (1160°C). The liquid atomic number density is denoted  $n_0$ ;  $\alpha = n_0^{-1/3}$ .