

Monte Carlo study of liquid GaAs: Bulk and surface properties

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We model the bulk and surface behavior of liquid GaAs, using a combination of two-body and three-body potentials of the form proposed by Stillinger and Weber. Following our recent work on CdTe, we fit the parameters of the potential to bulk and molecular atomization energies, lattice constants, and melting temperatures. The calculated pair radial distribution agrees very well with experiment. The elastic constants, surface tension, and heat of fusion also show reasonable agreement with reported experimental values.

I. INTRODUCTION

In a recent publication,¹ Wang, Stroud, and Markworth calculated the bulk and surface properties of liquid CdTe, using empirical two-body and three-body potentials of the form originally proposed by Stillinger and Weber.² They fitted the parameters of the potentials to bulk atomization energies of the elements, the lattice constants of the elements and the compound, the melting temperature of the compound, and the heat of formation of the compound from its constituents. The resulting potentials, when used in a Monte Carlo simulation, were found to give very good agreement with many measured properties of both solid and liquid CdTe at stoichiometry, including the surface tension, the heat of fusion, the elastic constants of the solid, and the structure factor of the liquid phase.

In this Brief Report, we extend the model of Ref. 1 to stoichiometric GaAs. Like CdTe, GaAs is of great technological importance. Since crystalline GaAs is usually grown from the melt, its liquid-state properties are of particular interest. At the same time, because of the high melting point of GaAs, they are rather difficult to measure accurately. The surface tension, and particularly its temperature derivative, are of special importance in microgravity environments. Under such conditions, surface-tension-driven convection is believed dominant, because conventional gravity-driven convection is suppressed.

II. MODEL

Our potentials have been described in our previous paper on stoichiometric CdTe.¹ To determine the parameters of the potential, we use the same fitting procedure as for CdTe, with one exception involving the As-As pair potential. Our previous method would have involved the fitting of this pair potential to the nearest-neighbor distance of a fictitious elemental As solid of the same density as solid As, but arranged in diamond lattice. This distance can be deduced from the lattice constant of elemental As.³ When applied to GaAs, the resulting As-As potential leads to pair distribution functions which differ

greatly from experiment. We have therefore fitted the parameters A and B of this potential, which govern the depth and the position of the minimum, to the As—As bond length as quoted in Ref. 4. This length is close to those of both the As_4 molecule and the Ga—As bond in the solid compound semiconductor.

The resulting constants A , B , and λ characterizing the two-body and three-body potentials are listed in Table I. The remaining constants (all defined in Ref. 1) are $\epsilon = 1.63$ eV, $\sigma = 2.183$ Å, $a = 1.80$, and $\nu = 1.20$. All parameters are dimensionless except ϵ and σ . The constant λ measures the strength of the three-body potential and is fitted, as in our previous work on CdTe, to the melting temperature T_m at one atmosphere of pressure. T_m is in turn calculated as the arithmetic mean of the superheat-

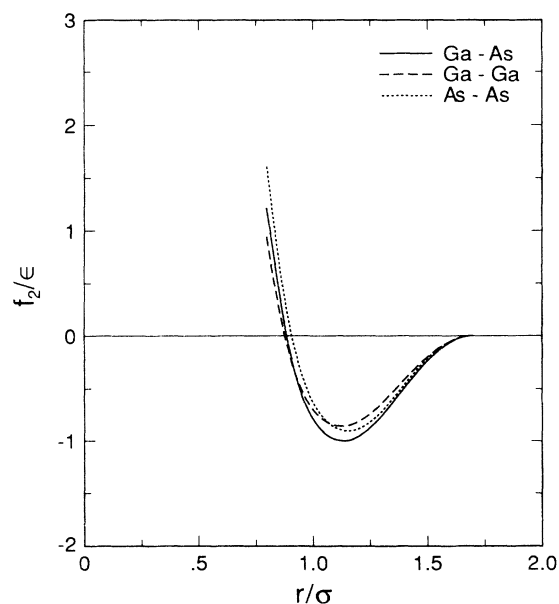


FIG. 1. Pair potentials $f_2(r/\sigma)$ for liquid and solid GaAs. The potentials are given in units of ϵ ; the particle separations in units of σ .

TABLE I. Parameters A , B , and λ for the two-body and three-body empirical potentials of solid and liquid GaAs. The parameters are defined in Ref. 1.

	Ga—As	Ga—Ga	As—As
A	7.0496	5.9768	6.8553
B	0.6022	0.5860	0.6711
λ	21	21	21

ing and supercooling limits. These are extracted from plots of the internal energy of the solid and the liquid, as calculated by Monte Carlo techniques on heating and on cooling.¹

Figure 1 shows a plot of the two-body potentials. All three potentials are quite similar. This is consistent with the fact that GaAs is a relatively nonpolar material, its ratio of heat of formation to cohesive energy being smaller than that of the more polar semiconductor CdTe.

III. RESULTS

Figure 2 shows the calculated and measured pair distribution functions $g(r)$ for liquid GaAs just above the melting temperature. $g(r)$ is the probability density for finding an atom (of either species) a distance r from the origin, given that there is an atom at the origin, and is normalized to unity at large r . The measured $g(r)$ is that of Bergman *et al.*,⁵ obtained by neutron diffraction. The calculated $g(r)$ is the result of averaging over 2000 Monte Carlo sweeps through the entire liquid of 216 atoms in a cell with periodic boundary conditions, after

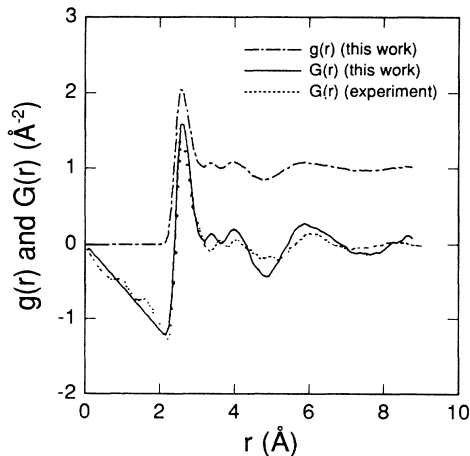


FIG. 2. Radial distribution functions for stoichiometric liquid GaAs. Dot-dashed curve, calculated $g(r)$ (a dimensionless quantity); solid line, calculated $G(r) = 4\pi\rho r [g(r) - 1]$ (in \AA^{-2}), ρ being the atomic number density of liquid GaAs. Both curves are obtained from Monte Carlo simulations at the melting temperature, $T = 1510$ K. Dotted line, $G(r)$ (in \AA^{-2}), as obtained from neutron-scattering data at temperature $T = 1523$ K (Ref. 5).

discarding the first 200 sweeps. Theory and experiment are in very good agreement. In particular, theory reproduces the height of the first peak, the split second peak, the dip near $r = 5$ Å, and the subsequent peak near $r = 6$ Å. The total number of nearest neighbors is defined as

$$N_{\text{NN}} = \int_0^{r_{\text{min}}} \rho g(r) (4\pi r^2) dr, \quad (1)$$

where ρ is the number density and $r_{\text{min}} \approx 3.14$ Å is the first minimum in $g(r)$ following the principle peak. We find $N_{\text{NN}} \approx 5.25$, in good agreement with the measured value of 5.5 ± 0.5 .⁶

The three calculated partial distribution functions $g_{\alpha\beta}(r)$, $\alpha, \beta = 1, 2$ are shown in Fig. 3 at $T = 0.08 \epsilon/k_B = 1510$ K. The $g_{\alpha, \beta}$'s are defined as the probability density for finding an atom of species α a distance r from the origin, given that there is an atom of species β at the origin, normalized to unity at large r . There are presently no experimental data with which these partial correlation functions can be compared. Zhang *et al.*⁶ have recently calculated the three $g_{\alpha\beta}(r)$'s using a first-principles molecular-dynamics method based on the approach of Car and Parrinello.⁷ This method, which includes both electronic and ionic degrees of freedom, gives $g_{\alpha\beta}$'s somewhat different from ours. In particular, whereas we find a large secondary peak in $g_{\text{Ga-Ga}}$ near $r = 4$ Å, Zhang *et al.* find such a peak in $g_{\text{As-As}}$.

We have also calculated the fraction of chemically "wrong" bonds using our empirical interactions. For Ga and As we find, respectively, 15 and 16% of such "wrong" bonds (i.e., 15% of Ga neighbors are Ga atoms, 16% of As neighbors are As atoms). Zhang *et al.* find 18 and 9% of such wrong bonds. The slightly lower fraction of Ga—Ga "wrong" bonds than that of As—As in our work is due to the fact that our empirical potential

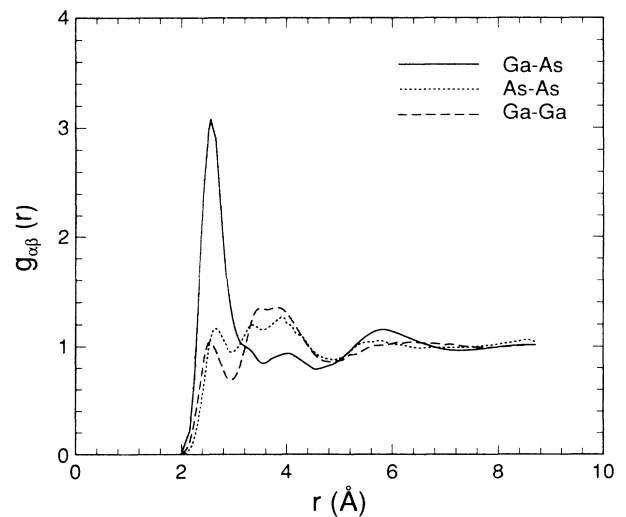


FIG. 3. Partial radial distribution functions $g_{\alpha\beta}(r)$ for stoichiometric liquid GaAs at $T = 1510$ K, as calculated via Monte Carlo simulation.

TABLE II. Calculated and measured properties of liquid and solid GaAs. The calculated elastic moduli, C_{11} , C_{12} , and C_{44} , are evaluated at room-temperature density and in units of 10^{11} dyn/cm². The heat of fusion, ΔH_f , is given in kcal/mol. The bulk and surface specific heats at melting temperature, $(C_v)_{\text{liq}}$ and $(C_v)_s$, are given in units of k_B per atom. The surface tension, τ (in erg/cm²), and its temperature derivative $d\tau/dT$ (in erg/cm² K) are both evaluated at the melting temperature.

	C_{11}	C_{12}	C_{44}	ΔH_f	$(C_v)_{\text{liq}}$	$(C_v)_s$	τ	$d\tau/dT$
This work	11.24	5.07	3.75	14.9	3.6	3.8	630	-0.24
Expt.	11.81 ^a	5.32 ^a	5.92 ^a	25.2 ^b			421 ^c	

^aReference 13.

^bReference 15.

^cReference 14.

for Ga—Ga is weaker than that of As—As. Another recent study of the structure of liquid GaAs was carried out by Hafner and Jank.⁸ They did a molecular-dynamics simulation using pseudopotential-derived interatomic potentials. They find an arrangement of atoms which is chemically quite random just above melting, with a larger fraction of “wrong” bonds than that found in either our work or that of Zhang *et al.* On the other hand, our total $g(r)$ seems to be in slightly better agreement with experiment than is either of the other two calculations. We conclude that our empirical potentials are reasonable for applications to stoichiometric liquid GaAs, but that they may need to be refined in the light of possible future measurements of the $g_{\alpha\beta}$'s in this material.

We have calculated several additional properties of liquid and solid GaAs using our empirical potentials. The calculated surface tension, its temperature derivative, the elastic constants of the solid state, and the heat of fusion are shown in Table II. All are obtained using the method described in Refs. 1 and 9, except for $d\tau/dT$. This derivative was obtained by a direct Monte Carlo evaluation of the surface tension at two different temperatures in a single Monte Carlo run, using the technique recently described by Ferrenberg and Swendsen.¹⁰ Such a method has recently been applied to liquid Si, and shown to give a much more accurate value of $d\tau/dT$ than numerical differentiation.¹¹

Both τ and $d\tau/dT$ are calculated by a two-step process described in Refs. 9 and 12. In the first step, periodic boundary conditions are replaced by hard-wall boundary conditions on two opposite faces of the cubic Monte Carlo cell. In the second step, these two hard walls are

moved to infinity, creating two free surfaces. The surface tension is the sum of the work per unit area required to carry out these two steps. In our GaAs calculations, we have found that about 20% of τ and about 65% of $d\tau/dT$ comes from step 2. These proportions are similar to what we found for liquid Si.

Our results generally agree well with available experiment. The elastic constants are in very good agreement with measured values,¹³ except for C_{44} , which is somewhat too low. This discrepancy is consistent with that found for calculations of the shear modulus in Si, using empirical potentials. The surface tension is 50% higher than the reported experimental value.¹⁴ The measured result dates from 1965, however, and should probably be viewed with some caution (the reported measurement for liquid Si, by the same authors, is about 20% below the currently accepted value of 885 dyn/cm). Our calculated heat of fusion deviates from the reported experimental value by about 40%.¹⁵ We could find no reports of measurements for $d\tau/dT$, but our value is similar to those reported for other compound liquid semiconductors.

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¹Z. Q. Wang, D. Stroud, and A. J. Markworth, Phys. Rev. B **40**, 3129 (1989).

²F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5265 (1985).

³C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976), p. 32.

⁴*CRC Handbook of Chemistry and Physics*, 68th ed., edited by R. C. Weast (CRC, Boca Raton, 1987), F-161.

⁵C. Bergman, C. Bichara, P. Chieux, and J. P. Gaspard, J. Phys. Colloq. **46**, C8-97 (1985).

⁶Q. M. Zhang, G. Chiarotti, A. Selloni, R. Car, and M. Parrinello, J. Non-Cryst. Solids **117/118**, 930 (1990).

⁷R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

⁸J. Hafner and W. Jank, J. Phys. Condens. Matter **1**, 4235 (1989).

⁹Z. Q. Wang and D. Stroud, Phys. Rev. B **38**, 1384 (1988).

¹⁰A. M. Ferrenberg and R. H. Swendsen, Phys. Rev. Lett. **61**, 2635 (1988).

¹¹Z. Q. Wang and D. Stroud, Phys. Rev. A **41**, 4582 (1990).

- ¹²J. Miyazaki, J. A. Barker, and G. M. Pound, *J. Chem. Phys.* **64**, 2264 (1976).
- ¹³Walter A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1979), p. 196.
- ¹⁴V. V. Karatavev, M. G. Mil'vidskii, and N. Ya. Zakharova, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **2**, 833 (1966).
- ¹⁵B. D. Lichter and P. Sommelet, *Trans. AIME* **245**, 1021 (1969).