

## MOLECULAR DYNAMICS SIMULATION OF ENTROPY AND SURFACE TENSION FOR GRAIN BOUNDARY OF $\alpha$ -Fe\*

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**ABSTRACT:** The grain boundary is an interface and the surface tension is one of its important thermodynamic properties. In this paper, the surface tension of the  $\Sigma 9$  grain boundary for  $\alpha$ -Fe at various temperatures and pressures is calculated by means of Computer Molecular Dynamics (CMD). The results agree satisfactorily with the experimental data. It is shown that the contribution of entropy to surface tension of grain boundary can be ignored.

**KEY WORDS:** grain boundary, entropy, surface tension, computer molecular dynamics simulation,  $\alpha$ -iron

### I. INTRODUCTION

The surface tension of grain boundary is a characteristic property. Computer simulation has been applied to grain boundaries only recently. There are many advantages in using the molecular dynamics for investigating the surface properties. For example, it can avoid the traditional experimental difficulties, and can investigate at atomistic level.

In this paper, we shall calculate the surface tension of grain boundary for  $\alpha$ -Fe by means of Computer Molecular Dynamics (CMD) and discuss the temperature and pressure effects.

Our results agree satisfactorily with the experimental data, and show that the contribution of entropy to surface tension of grain boundary is quite small.

### II. THE COMPUTATIONAL METHOD

For the one-component system,  $U$ ,  $S$ ,  $V$  are used to express the total internal energy, entropy and volume for the heterogeneous crystal, respectively. The internal energy can be written as

$$U = TS - PV + GA \quad (1)$$

where  $T$  is the temperature,  $P$  the pressure and  $G$  and  $A$  are the surface tension and area of grain boundary. For the single crystal at the same  $T$  and  $P$ , which is taken as a reference system, we have

$$U_0 = TS_0 - PV_0 \quad (2)$$

From Eqs. (1) and (2), we obtain

$$G = \frac{1}{A} [(U - U_0) - T(S - S_0) + P(V - V_0)] \quad (3)$$

In order to investigate the effects of temperature on the surface tension for a two-phase system, we need not only to calculate the surface excesses of  $U$  and  $V$ , but also to include the effect of entropy. In the CMD, the internal energy  $U$  can be obtained from knowledge of the configuration, potential energy function and the kinetic energy and the pressure  $P$  is obtained directly from the configuration by means of the virial. We shall briefly describe the calculation of entropy in CMD as follows.

From the thermodynamics,  $dU = TdS - PdV$ , we obtain

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$$S_2 = S_1 + \int_1^2 (dU/T) + \int_1^2 PdV/T \quad (4)$$

In order to calculate  $S_2$ , we need not only to calculate the  $U$ ,  $P$ ,  $V$ ,  $T$  from the configuration, potential function and the kinetic energy, but also to obtain the absolute entropy  $S_1$  at a reference temperature.

Theoretically, we must take absolute zero temperature as the reference temperature. However, it is impossible to do so in a classical CMD calculation. A compromise is to choose a reference temperature which is low enough so that a perfect model (e. g., harmonic oscillator model) can be used, and at the same time, which is high enough so that the quantum effects are quite small and the system can be considered as a classical one. Usually, Debye temperature of the crystal is taken as the reference temperature.

After choosing the reference temperature, the classical entropy of the system with  $N$  atoms at temperature  $T$  is expressed as<sup>[1]</sup>

$$S = 3Nk \int_0^{\omega_L} d\omega g(\omega) \{1 - \ln(\hbar\omega/kT)\} \quad (5)$$

where  $g(\omega)$  is normalized

$$\int_0^{\omega_L} d\omega g(\omega) = 1 \quad (6)$$

where  $\hbar = h/2\pi$ ,  $h$  is the Plank constant,  $k$  the Boltzmann's constant, and  $g(\omega)$  is frequency distribution. In the system, we assume that  $g(\omega)$  is independent of temperature. It is equivalent to assuming that atoms in the system are harmonic oscillators.

We use the method of velocity autocorrelation function<sup>[1]</sup> to calculate  $g(\omega)$

$$g(\omega) = \frac{M}{3kNT} \sum_{i=1}^N \frac{2\pi}{\Delta t} |v_i(\omega)|^2 \quad (7)$$

$$v_i(\omega) = \int_0^\infty dt e^{i\omega t} v_i(t) \quad (8)$$

where  $M$  is the mass of atom,  $\Delta t$  the time step in the simulation, and  $v_i$  the velocity of atom  $i$ . The velocity evolution  $v_i(t)$  can be transformed into  $v_i(\omega)$  by means of the Fourier transformation. After obtaining  $g(\omega)$ , the reference entropy is calculated by Eq.(5). Then, the entropies at various temperatures are calculated by Eq.(4) and the surface tension  $G$  can be obtained from  $U$ ,  $S$ ,  $V$  and  $T$ ,  $P$ ,  $A$  by using Eq.(3).

### III. COMPUTATIONAL PROCEDURE

The model block of heterogeneous crystal is shown in Fig.1. The rotational axis of  $\Sigma 9$  grain boundary in  $\alpha$ -Fe is  $[110]$ , the boundary surface  $(\bar{1}\bar{1}4)$  and the rotational angle  $38.94^\circ$ .

The periodic boundary conditions in  $Y$ ,  $Z$  directions are used and a fixed boundary in  $X$  direction is used. The number of movable atoms is 528 (part A in Fig.1) and the number of fixed atoms 80 (part B in Fig.1). The model block of the single crystal is smaller and the numbers of atoms are 210 and 60, respectively. The classical Newton equations are used to describe motions of the atoms

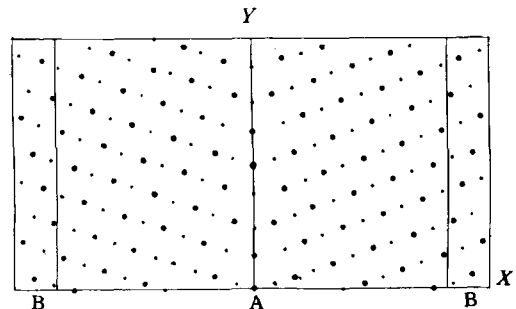


Fig.1 The model block of  $\Sigma 9$  grain boundary for  $\alpha$ -Fe after rotation  $38.94^\circ$  about a  $[110]$  axis. The boundary surface is  $(\bar{1}\bar{1}4)$ .

$$F_i = M \frac{d^2 R_i}{dt^2} \quad (i=1, 2, \dots, N) \quad (9)$$

where  $R_i$  is the coordinate vector of atom  $i$ ,  $F_i$  is the resultant force acting on  $i$ ,  $M$  the atomic mass, and  $N$  the total number of atoms.  $F_i$  can be obtained from interaction potential  $V$

$$F_i = - \sum_{j \neq i} \frac{\partial V(R_{ij})}{\partial R_{ij}} \frac{R_{ij}}{R_{ij}} \quad (10)$$

where  $R_{ij}$  is the separation distance between atom  $i$  and  $j$  and  $R_{ij}$  vector displacement of atom  $i$  with respect to atom  $j$ . The  $3N$ -dimensional equations for  $N$  atoms are solved by using the central difference method.

We assume that interactions of these atoms are pair-wise additive. Johnson's four-parameter pair-potential<sup>[2]</sup> is used

$$V(R_{ij}) = -C_1 (R_{ij} - C_2)^3 + C_3 R_{ij} - C_4 \quad (11)$$

where  $V$  is a function of  $R_{ij}$  with constants  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  which are different in various ranges (see Table 1). The units of  $V$  and  $R_{ij}$  are electron-volt (eV) and Angstrom ( $\text{\AA}$ ), respectively.

We use the dimensionless formulas in which the unit of energy is potential depth ( $=4.03142 \cdot 10^{-13}$  erg.); the unit of length is a function of temperature  $a_t (=a_0 [1 + \alpha(T - 293.16) + \beta(T - 293.16)^2])$ , where  $a_0 = 2.86645 \cdot 10^{-8}$  cm,  $\alpha = 1.145 \cdot 10^{-5}$ ,  $\beta = 7.10 \cdot 10^{-9}$ ; the unit of time is  $4.35574 \cdot 10^{-13}$  s and the unit of mass is  $9.26967 \cdot 10^{-23}$  g. In calculations,  $\Delta t = 0.01$ , the semifixed neighbor method is used and truncation distances  $R_c = 1.2$ ,  $R_{\max} = 1.4$  (see Ref.[3]). In the computations, the neighbor list is compiled once per 50 steps, and the temperature and pressure are adjusted per 1000 steps. The pressure is adjusted in terms of compressibility  $-(1/V)(\Delta V/\Delta P)_T = 0.6 \cdot 10^{-6}$  /atm. Error of the calculated pressure is less than  $\pm 200$  atm.

Table 1  
The Johnson's potential constants for iron  
(R is in unit of  $\text{\AA}$  and  $V$  in unit of eV)

R	$C_1$	$C_2$	$C_3$	$C_4$
1.9—2.4	2.195976	3.097910	2.704060	7.436448
2.4—3.0	0.639230	3.115829	0.477871	1.581570
3.0—3.44	1.115035	3.066403	0.466892	1.547967

#### IV. RESULTS AND DISCUSSIONS

The Debye temperature of  $\alpha$ -Fe is 453 K. In this paper, we take 460 K as the reference

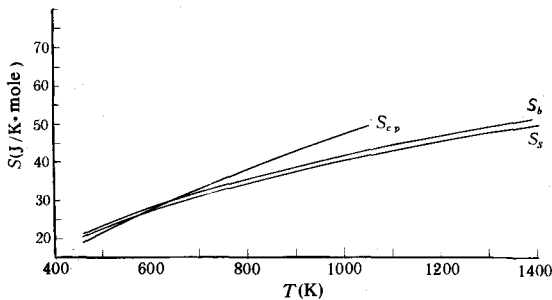


Fig. 2 Entropy  $S$  vs temperature  $T$  at  $P=1$  atm.  $S$  in unit of  $\text{J}/\text{mole} \cdot \text{K}$ .  $S_b$  is entropy of the heterogeneous crystal,  $S_s$  is one of the single crystal and the  $S_{cp}$  is the calorimetry entropy.

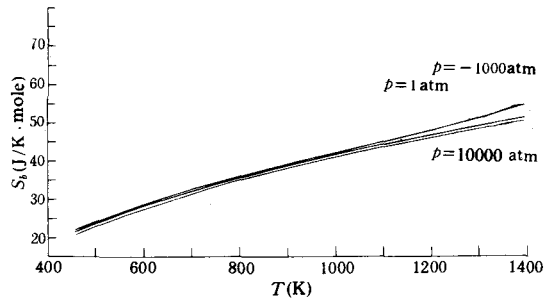


Fig. 3  $S$  vs  $T$  for the heterogeneous crystal at various pressures. Pressure is in unit of atm. and entropy in unit of  $\text{J}/\text{mole} \cdot \text{K}$ .

temperature. The temperature range for calculating entropy and surface tension is 460 ~ 1400 K and the pressure may be up to  $10^4$  atm.

Fig.2 shows the variation of entropy with temperature at ambient pressure, where  $S_b$  is entropy of grain boundary in heterogeneous system,  $S_s$  is reference entropy at the same pressure,  $S_{cp}$  is  $\alpha$ -Fe entropy obtained by means of calorimetry method<sup>[5]</sup> from the data of specific heat at constant pressure<sup>[4]</sup>. It is noted that the computational results of CMD are in satisfactory agreement with those obtained in experiments. The entropy increases with temperature, but  $S_b$  and  $S_s$  increase slower than  $S_{cp}$  does. Fig.3 shows values of  $S_b$  at difference pressures. It is shown that the effect of pressure on the entropy is weak. It is similar for  $S_s$  of the single crystal.

Fig.4 shows the isobars of surface tension  $G$  which increases with temperature. When pressure increases,  $G$  increases rapidly. By means of the least square regressive method, polynomials of temperature at various pressures are obtained

$$G(T) = a + bT + cT^2 + dT^3 \quad (12)$$

The coefficients in Eq.(12) at various pressures are shown in Table 2.

**Table 2**  
The coefficients of least square regressive polynomial at various pressures for the surface tension of  $\Sigma^9$  grain boundary for  $\alpha$ -Fe

$P$ (atm)	$a$	$b$	$c$	$d$
-1000	$0.92227 \times 10^3$	0.64369	$-0.15916 \times 10^{-3}$	
1	$0.62044 \times 10^3$	2.03550	$-0.21424 \times 10^{-3}$	$0.94844 \times 10^{-6}$
10000	$0.96430 \times 10^3$	1.40557	$-0.94754 \times 10^{-3}$	$0.51816 \times 10^{-6}$

It is noted from Eq.(3) that contributions to the surface tension of grain boundary in a one-component system are from three parts: excesses of internal energy ( $U - U_0$ ), entropy ( $S - S_0$ ), and volume ( $V - V_0$ ). Computational results show that the contribution of ( $V - V_0$ ) increases with pressure while one of ( $S - S_0$ ) is quite small and almost constant. For example, when  $P = 1$  atm, the contribution of ( $V - V_0$ ) at different temperatures are  $3 \times 10^{-4}$ — $4 \times 10^{-4}\%$ . However, when  $P = 10^4$  atm the contributions are 17 — 28%. The contribution of  $S - S_0$  is less than  $1 \times 10^{-4}\%$  at different temperatures and pressures. Hence, even if  $T \neq 0$ , the contribution of entropy to surface tension of grain boundary can be ignored.

Since effect of volume at the ambient pressure is week, the surface tension is almost equal to the free energy of surface. In Fig.4 experimental data of surface free-energy from two different sources<sup>[6,7]</sup> are shown as well. It is noted that they are in good agreement with the extrapolated values of the curve at ambient pressure. The surface free-energy at high pressure is closely related with the ( $V - V_0$ ) term. It seems that the free volume of atoms at grain boundary is different from that in the single crystal. In this paper, only the pair-wise additive potential is used and the effects of multi-body potential are not included. Although this approximation is not perfect, it is thought that its effect is in the order of magnitude less than that of volume, so that our results are still reliable.

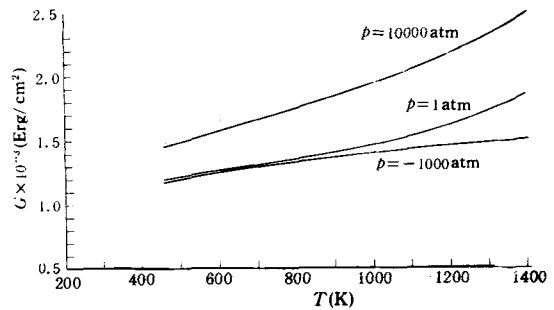


Fig.4 Surface tension  $G$  vs temperature  $T$  at various pressures.  $G$  is in unit of  $\text{erg}/\text{cm}^2$

## REFERENCES

- [ 1 ] Harrison Ralph J., Cox J. A., Bishop G. H. and Yip Sidney, in International Conference on Computer Simulation for Materials Applications, ed. by Arsenault R.J., Beeler, Jr. J. R. and Simmons J. A., **20**, part I, 325.
- [ 2 ] R. A., Johnson, *Phys. Rev.* **134**, 5A (1964), A1329.
- [ 3 ] Ding Jiaqiang, Chen Zhiying, Semi-fixed neighbor method of molecular dynamics simulation for solid state, *Mechanics and Practice* **3** (1989), 39 (in Chinese).
- [ 4 ] Baron H. M., Covnit E.H. et al., Brief Handbook of Data in Physics and Chemistry, Science and Technology Press (in Chinese, translated from Russian) (1956).
- [ 5 ] Tang Youqi, Statistical Mechanics and Its Applications in Physical Chemistry, Science Press (1979) (in Chinese).
- [ 6 ] Inman, M. C., and H. R. Tipler, Interfacial energy and composition in metals and alloys, *Met. Review*, **8**, 105 (1963).
- [ 7 ] Friedel, J., Dislocations, Pergamon Press, Oxford (1964), 275.