

MOLECULAR DYNAMICS SIMULATION OF THERMOPHYSICAL PROPERTIES OF UNDERCOOLED LIQUID COBALT¹

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ABSTRACT

Molecular dynamics simulations based on embedded-atom-method (EAM) are applied to calculate the density, specific heat and self-diffusion coefficient of liquid cobalt at temperatures above and below the melting temperature. Simulations indicate that the density fits into $\rho = 7.47 - 7.6 \times 10^{-4}(T - T_m)$ gcm⁻³, and the self-diffusion coefficient is given by $D = 63.9678 \exp(-40843.03/RT)$ m²/s. Dissimilar to the linear dependence of the density and the Arrhenius dependence of the self-diffusion coefficient on temperature, the specific heat shows almost a constant value of 32.509±0.194 J/mol/K within the temperature range of simulation. Calculations of the self-diffusion coefficient also indicate that the Green-Kubo expression and the generalized Einstein equation produce the close results. The simulated properties of liquid cobalt are compared with some experimental data and the estimated values from empirical expressions at temperatures above the melting point. Comparisons show reasonable agreements.

KEY WORDS: density; liquid metal; molecular dynamics simulation; self-diffusion coefficient; specific heat

1. INTRODUCTION

Specific heat, density and self-diffusion coefficient are of especial interest in the fields of materials science, applied physics, and fluid science^[1-3]. With these three parameters in undercooled regime, one can quantitatively predict the processes of crystal nucleation and crystal growth during rapid solidification^[4,5]. Furthermore, the knowledge of these three parameters in the undercooled region can also reveal the local structure of the undercooled liquid^[6], and thus be used to predict the glass transition trend of metallic melts^[7] and to determine the ideal glass transition temperature^[8]. However, for liquid metals, due to the experimental difficulties in dealing with the metastable state of undercooled melts at high temperatures, there are few experimental data of these three parameters in undercooled regime available. The accuracy knowledge of the thermophysical properties not only demands the further development of experimental techniques, such as the containerless processing technique in

combination with non-contact diagnostic method, but also demands the development of reliable predictive methods.

Molecular dynamics simulation (MDS) with a potential model from the embedded-atom-method (EAM) is proved to be a powerful approach to the simulation of liquid metals, which was developed two decades ago and has been successfully applied to simulate the structure, surface, dislocation, and phase transformation of solid or liquid metals^[9-11]. It was also applied to predict thermophysical properties of liquid metals at some extreme cases^[12,13].

Cobalt is a ferromagnetic transition metal with wide applications in the aerospace industry. Nevertheless, there is a lack of experimental data of specific heat, density and diffusion coefficient, especially in the undercooled region. The purpose of this paper is to carry out simulations on these three parameters, especially in the undercooled region. The experimental data available are used for comparisons.

2. EMBEDDED-ATOM METHOD

The embedded-atom method (EAM) is a semi-empirical technique for computing the energy of an arbitrary arrangement of atoms. According to the EAM potential model originally developed by Daw and Baskes on the basis of the density function theory^[14,15], the energy of an atomic system can be written as

$$E_{tot} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{i \neq j} \phi_{i,j}(r_{i,j}) \quad (1)$$

$$\rho_i = \sum_{i \neq j} f_j(r_{i,j}) \quad (2)$$

where F_i is the energy for embedding atom i in an electron density ρ_i , $\phi_{i,j}$ a repulsive two-body potential between atoms i and j , and $f_j(r_{i,j})$ the contribution of atom j to the electron density at atom i at a distance $r_{i,j}$ from atom j .

According to Johnson^[16], $F(\rho)$, $\Phi(\rho)$, and $f(r)$ are expressed as:

$$f(r) = f_e \left(\frac{b}{r} \right)^\beta \quad (3)$$

$$\phi(r) = 2\gamma \cdot E_c \left[\frac{1}{\gamma \cdot S_\gamma} \left(\frac{b}{r} \right)^\gamma - \frac{1}{\beta \cdot S_\beta} \left(\frac{b}{r} \right)^\beta \right] \quad (4)$$

$$F(\rho) = -E_c \left\{ 1 + \alpha \left[\left(\frac{\rho_e}{\rho} \right)^{1/\beta} - 1 \right] \right\} \cdot \exp \left[-\alpha \left(\frac{\rho_e}{\rho} \right)^{1/\beta} - 1 \right] - E_c \left[\left(\frac{\rho}{\rho_e} \right)^{\gamma/\beta} - \frac{\gamma}{\beta} \frac{\rho}{\rho_e} \right] \quad (5)$$

with

$$f_e = \frac{E_c}{S_\beta \Omega} \quad (6)$$

$$S_\beta = \sum_{i=1}^n N_i \left(\frac{r_i}{b} \right)^{-\beta} \quad (7)$$

$$S_\gamma = \sum_{i=1}^n N_i \left(\frac{r_i}{b} \right)^{-\gamma} \quad (8)$$

where E_c is the cohesive energy, b the nearest neighbor distance, Ω the unit cell volume, and r_i, N_i the radius and the number of atoms in the i th neighbor shell.

All of the model parameters used during simulations are listed in table 1 ^[17].

Table 1. The model parameters

Model parameter								
$b(\text{\AA})$	$\Omega (\text{\AA}^3)$	ρ_e	f_e	S_γ	S_β	γ	β	α
2.503	11.09	0.3956	0.02849	12.806	13.886	7.745	5.933	5.004

3. SIMULATION DETAILS

The density and specific heat are simulated applying MD simulation method under constant pressure and constant temperature (NPT ensemble). During simulation, the pressure is set to zero. At the beginning of the simulation, 500 atoms were arranged in a face-centered cubic box subject to periodic boundary conditions in three directions. The time step was 3.92×10^{-15} s. In order to get equilibrium liquid state in the simulation, the system started at 2000 K, which is well above the melting point. This temperature was kept constant for 50,000 steps. Then the quenching process with a cooling rate of $5 \times 10^{11} \text{ K} \cdot \text{s}^{-1}$ was carried out to calculate the enthalpy H and density ρ at 100 K intervals of temperature. At each temperature, 30,000 steps were carried out for equilibrium. Then 20,000 additional steps were taken to calculate the enthalpy and density. The simulation was stopped at 1200 K, which is 576 K lower than the melting point. Since the quenching process is very fast, the metal stays in undercooled liquid state.

The density can be derived from the Virial expression of pressure ^[18]:

$$\begin{aligned} PV &= Nk_B T + \frac{1}{3} \left\langle \sum_{i<j} r_{ij} \cdot f_{ij} \right\rangle \\ &= \frac{\rho}{M_A} V k_B T + \frac{1}{3} \left\langle \sum_{i<j} r_{ij} \cdot f_{ij} \right\rangle \end{aligned} \quad (9)$$

where N is the number of atoms, ρ the density, M_A the absolute mass of one atom, V the volume of the simulated liquid metals, k_B Boltzmann constant, T the temperature, f_{ij} the force between atom i and atom j , and $\langle \rangle$ ensemble average.

Specific heat can be determined from the differential of the enthalpy:

$$C_p = \frac{dH(T)}{dT} \quad (10)$$

As to the self-diffusion coefficient D , there are two calculation methods^[18]. One is to calculate from the Generalized-Einstein (GE) equation

$$D = \lim_{t \rightarrow \infty} \frac{1}{6Nt} \left\langle \sum_{j=1}^N [r_j(t) - r_j(0)]^2 \right\rangle \quad (11)$$

where $r_j(0)$ is the initial position of j th particle, and $r_j(t)$ the position of j th particle at some later time t .

The other method is to calculate the self-diffusion coefficient from the Green-Kubo equation (GK):

$$D = \frac{1}{3N} \int_0^{\infty} \left\langle \sum_{j=1}^N \vec{v}_j(0) \cdot \vec{v}_j(\tau) \right\rangle d\tau \quad (12)$$

where $\vec{v}_j(0)$ is initial velocity vector for the j th particle, and $\vec{v}_j(\tau)$ the velocity vector at some later time τ .

The simulations of self-diffusion coefficient were run using a microcanonical ensemble (constant N , V and E). The volume was selected in such a way that the average pressure equaled zero. In order to obtain reliable average values for Eqs. (11) and (12), we utilized the algorithm of overlapping-time-interval correlation averages proposed by Rapaport^[18]. The results for the self-diffusion coefficient was calculated using an average of 600 individual correlation functions spaced 0.012 ps. For each autocorrelation function calculated, the simulations lasted approximately 10 ps. To improve the quality of the results, each computation is run for about 600,000 time steps, which yields 15 sets of autocorrelation results.

4. SIMULATION RESULTS

Fig. 1 presents the relationship between the density obtained from simulation and the temperature for pure liquid cobalt in the temperature range from 1200 to 2000K, which corresponds to a undercooling of 576K ($0.324T_m$) and a superheating of 232K. A linear regression analysis of the data gives:

$$\rho = 7.47 - 7.6 \times 10^{-4} \cdot (T - T_m) \quad \text{g cm}^{-3} \quad (13)$$

The experimental data from *Smithells Metals reference book*^[19] were also added to Fig.1, which are represented by:

$$\rho = 7.76 - 9.88 \times 10^{-4} \cdot (T - T_m) \quad \text{g cm}^{-3} \quad (14)$$

Comparison indicates that the simulated density is slightly lower than the experimental data. The difference is within 3-4%. Owing to the lack of density data in

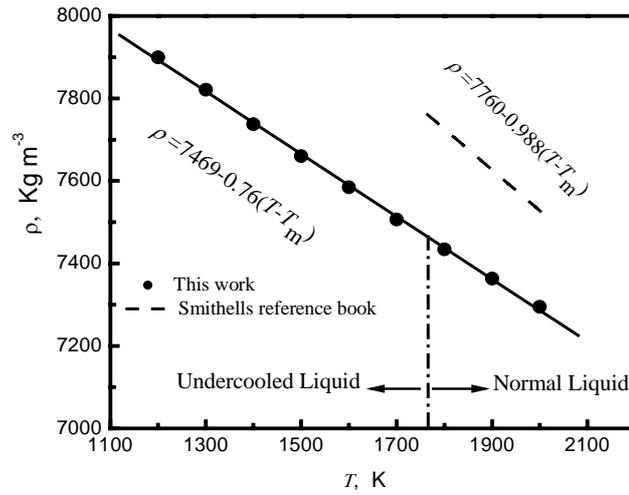


Fig.1 Density of liquid cobalt versus temperature.

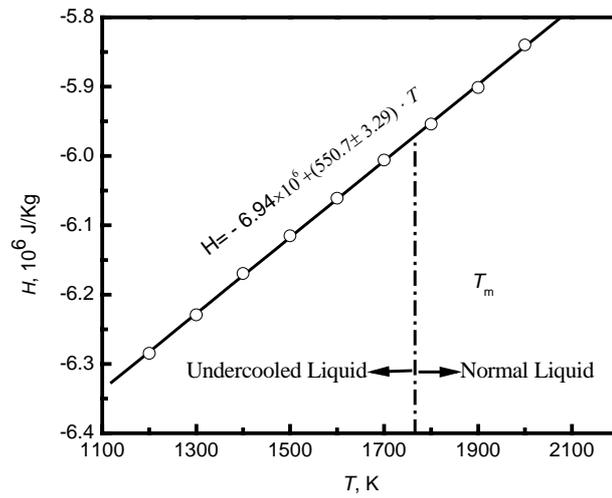


Fig. 2 Calculated enthalpy of liquid cobalt versus temperature.

the undercooled regime, the deviation between the simulated and measured density below the melting point cannot be evaluated.

The simulation results for the enthalpy H are shown in Fig. 2. Apparently, the enthalpy has a linear dependence of temperature. Data analysis shows that

$$H = -6.94 \times 10^6 + (550.7 \pm 3.29) \cdot T \text{ J/kg} \quad (15)$$

This means that the heat capacity is a constant $32.509 \pm 0.194 \text{ J mol}^{-1} \text{ K}^{-1}$ in the temperature range of 1200-2000 K. This result is close to the experimental data of $34.8 \text{ J mol}^{-1} \text{ K}^{-1}$ from *Smithells Metals reference book*, but about 19% lower than $40.38 \text{ J mol}^{-1} \text{ K}^{-1}$ above the melting point^[20], and $40.6 \text{ J mol}^{-1} \text{ K}$ in the undercooled regime^[4].

Fig.3 illustrates the simulation results for the self-diffusion coefficient from Einstein

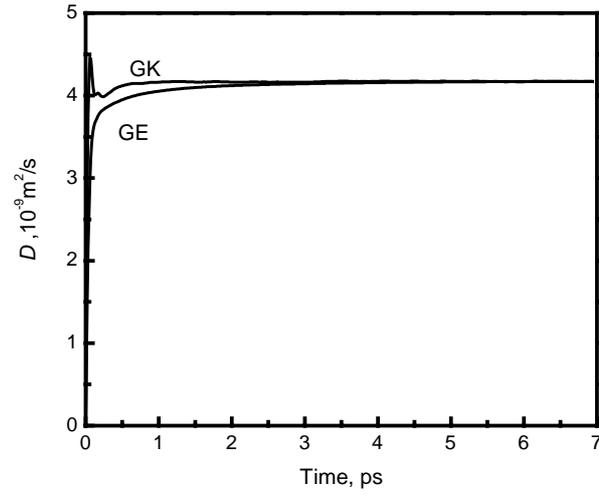


Fig. 3 Calculated self-diffusion coefficient at 1800K from generalized Einstein equation and Green-Kubo expression

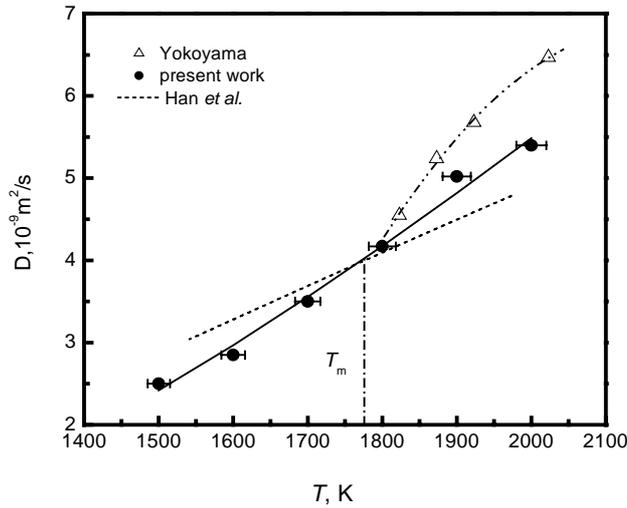


Fig. 4 Dependence of self-diffusion coefficient on temperature.

equation and Green-Kubo expression at 1800K. When the correlation time exceeds about 3ps, Green-Kubo expression and the generalized Einstein equation produce similar results. Shown in Fig. 4 are the results of the self-diffusion coefficient of liquid cobalt as a function of temperature. The solid circles are the data calculated in current simulation, which are expressed as:

$$D = 63.9678 \exp\left(-\frac{40843.03}{RT}\right) \text{ m}^2/\text{s} \quad (16)$$

where R is the gas constant, 8.314J/mol/K.

In Fig. 4, the open triangles represent the self-diffusion coefficients predicted by Yokoyama^[21], and the short dash represents the results predicted from viscosity data by

Han *et al.* according to Stokes-Einstein expression ^[22]. It can be seen that the simulation results in this work lie within the data predicted by Yokoyama and Han *et al.* from empirical expressions. At the vicinity of the melting point, the self-diffusion coefficients obtained in this work are in good agreement with the predicted values of Yokoyama and Han *et al.*. Nevertheless, when the temperature is far from the melting point, the simulated self-diffusion coefficients deviate from the predicted values. Moreover, the larger is the difference between the temperature and the melting point, the larger is the deviation between the simulated and predicted data. At 2000K, the simulated self-diffusion coefficient is about 10% larger than Han's value and about 10% smaller than Yokoyama's value.

5 CONCLUSIONS

Density, specific heat, and self-diffusion coefficient of liquid cobalt at a wide temperatures range, especially in the undercooled regime have been predicted with molecular dynamics simulations based on embedded-atom-method (EAM). At temperatures of 1200-2000K, the densities are predicted by $\rho = 7.47 - 7.6 \times 10^{-4}(T - T_m)$ g cm⁻³, which are in good agreement with experimental results above the melting point, within a deviation of 4%. In the simulation temperature range, the self-diffusion coefficients show Arrhenius temperature dependence represented by $D = 63.9678 \exp(-40843.03/RT)$ m²/s, which agree well with the approximated values from empirical expressions at the vicinity of the melting point. Simulations of self-diffusion coefficient indicate that the generalized Einstein equation and Green-Kubo expression produce similar results when the autocorrelation time exceeds about 3ps. Compared with the density and self-diffusion coefficient, specific heat shows no obvious temperature dependence in the simulation temperature range. The predicted value of 32.509±0.194 J mol⁻¹ K⁻¹ reasonably agrees with the experimental results. Simulations show that molecular dynamics simulation method with EAM inter-atomic potential model can predict the thermophysical properties of undercooled liquid metals quantitatively.

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