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Wetting Behavior of Molten Ag Nanodroplet on the Cu Substrate

M. Goli*, J. Davoodi†

University of Zanjan, Zanjan, 45371-38791, Iran

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The main objective of this investigation was to study spreading of Silver (Ag) nanodroplet on the Cooper (Cu) surface by molecular dynamics (MD) simulation method. The quantum Sutton-Chen (Q-SC) many body potential was used to calculate cohesive energy as well as force experienced by every atoms. The temperature and pressure of nanodroplet were controlled by Nose-Hoover thermostat and Berendsen barostat respectively. The effect of nanodroplet size on the wetting and contact angle of silver nanodroplet on a copper solid surface was calculated by changing the number of atoms within the nanodroplet. By varying the cooling rate during spreading of nanodroplet, it was found that decreasing the cooling rate decreases the contact angle of nanodroplet, and it spreads better on the copper surface. Also, increasing initial temperature of nanodroplet decreased the contact angle.

Keywords: Ag Nanodroplet, Spreading, Molecular Dynamics Simulation, Cu Substrate

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1. INTRODUCTION

The spreading of droplet on the solid surfaces is very important due to its broad applications, including propulsion, surface coating, spray painting and cooling, ink-jet printing, and biological sensors [1]. Furthermore, molecular level understanding of dynamics of liquid and solid contact is important for phase change heat transfer such as evaporation and condensation [2]. Extensive studies have been carried out over the past few decades to investigate the wetting phenomena of a droplet on the different surface [3, 4].

In the soldering process, a metallurgical bond is formed between the molten solder and a metal substrate. So the capability of the molten solder to flow on the surface is very important for the formation of a suitable metallic bond. The process of spreading of molten droplet on surface defined as wetting. Contact angle, θ, is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, gas and solid intersect. This angle can also be considered in terms of the thermodynamics of the materials by Young-Dupre equation for the balance of surface tensions at the liquid-gas-solid three phase from the following form

$$\gamma_{gs} = \gamma_{ls} + \gamma_{gl}\cos\theta \,, \qquad (1.1)$$

where γ_{gs}, γ_{ls} and γ_{gl} refer to the surface tension or interfacial energies of the gas/solid, liquid/solid and gas/liquid interface respectively. There are different experimental method for measure contact angles, for instance, the wetting-balance [5] and sessile-drop techniques [6, 7] have been used extensively.

2. MD SIMULATION DETAILS

2.1 Interatomic Potential

In a classical MD simulation, the deterministic force experienced by

$$\vec{f}_i = -\sum_{j \succ i} \nabla_{r_i} U(r_{ij}) \,, \qquad (2.1)$$

where $U(r_{ij})$ is the inter-atomic potential and r_{ij} is the separation distance between two atoms i and j. The interatomic potential employed in this MD simulation is the quantum Sutton-Chen (Q-SC) many body potential [8, 9]

$$U_{tot} = \sum_{i=1}^{N}\left[\sum_{j\neq i}\varepsilon_{ij}\frac{1}{2}\left(\frac{a_{ij}}{r_{ij}}\right)^{n_{ij}} - c_i\varepsilon_{ii}\left(\sum_{j\neq i}\left(\frac{a_{ij}}{r_{ij}}\right)^{m_{ij}}\right)^{1/2}\right], \qquad (2.2)$$

The first term describes the pair interaction between atoms i and j, and the second term represents the many-body cohesive term associated with atom i. a is the parameter with dimensions of length, c is a dimensionless constant, ε is an energy parameter, and n, m are positive integers with $n \succ m$. The parameters pertinent to the metals considered in this paper, and obtained for the Q-SC potentials, are listed in Table 1. To construct the potential for the binary state, Ag-Cu, from the corresponding Q-SC potentials for the elemental metals, the following mixing rules [10] were employed:

$$\varepsilon_{ij} = (\varepsilon_i\varepsilon_j)^{1/2} \,, a_{ij} = (a_i a_j)^{1/2} \,, \qquad (2.3)$$

$$m_{ij} = (m_i + m_j)/2 \,, n_{ij} = (n_i + n_j)/2 \,, \qquad (2.4)$$

Table 1 – The Q-SC potential parameters for Ag and Cu

Metal	ε(eV)	*a*(Å)	*c*	*n*	*m*
Ag	0.003945	4.0691	96.52	11	6
Cu	0.005792	3.6030	84.84	10	5

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[*] m_goli@znu.ac.ir
[†] jdavoodi@znu.ac.ir

2.2 Temperature and Pressure Control

The temperature control was implemented via the Nose-Hoover thermostat whose introduction modifies the standard velocity Verlet equation of motion to the following form [11, 12]

$$\vec{r}_i(t+\delta t)=\vec{r}_i(t)+\delta t\bar{v}_i(t)+\frac{1}{2}\delta t^2\left[\frac{\vec{f}_i(t)}{m_i}-\zeta(t)\bar{v}_i(t)\right],$$

$$\bar{v}_i(t+\frac{1}{2}\delta t)=\bar{v}_i(t)+\frac{\delta t}{2}\left[\frac{\vec{f}_i(t)}{m_i}-\zeta(t)\bar{v}_i(t)\right]$$

$$\zeta(t+\tfrac{1}{2}\delta t)=\zeta(t)+\frac{\delta t}{2Q}\left[\sum_i^N m_i\vec{v}_i^2(t)-gk_bT\right] \tag{2.5}$$

$$\bar{v}_i(t+\delta t)=\frac{2}{2+\delta t\zeta(t+\delta t)}\left[\bar{v}_i(t+\tfrac{1}{2}\delta t)+\frac{1}{2}\delta t\frac{\vec{f}_i(t+\delta t)}{m_i}\right]$$

$$\zeta(t+\delta t)=\zeta(t+\tfrac{1}{2}\delta t)+\frac{\delta t}{2Q}\left[\sum_i^N m_i\vec{v}_i^2(t+\tfrac{1}{2}\delta t)-gk_bT\right]$$

where ζ is the friction of the heat bath. A particular parameterization of the Q is given by

$$Q=gk_bT\tau^2, \tag{2.6}$$

where g is the number of degrees of freedom and τ is the relaxation time of the heat bath, normally of the same order of magnitude as the simulation time step, δt. This parameter controls the speed with which the bath damps down the fluctuation in the temperature.

The Berendsen barostat [13] was used to control pressure of system. This barostat uses a scale factor, μ, which is a function of instantaneous pressure, P, to scale lengths in the system

$$\begin{aligned}x(i)&\to\mu x(i)\\ y(i)&\to\mu y(i)\\ z(i)&\to\mu z(i)\\ L&\to\mu L\end{aligned}, \tag{2.7}$$

where μ is given by

$$\mu=\left[1-\frac{\delta t}{\tau_p}(P-P_0)\right]^{1/3}, \tag{2.8}$$

Here, τ_p is the rise time of the barostat, and P_0 is the set point pressure. The system pressure is set toward a desired value by changing the dimensions of the simulation cell size during the simulation.

3. RESULTS AND DISCUSSION

The simulation involving nano sized cluster of Ag atoms and Cu substrate. The totals Number of atoms which are used in this simulation were 5438, 5683 and 6058 particles which 5000 particles were substrate and remain were nanodroplet. At first the solid Ag with face centered cubic (FCC) structure was melted with use of MD simulation and then released liquid nanodroplet on the substrate to spread droplet on the surface (Fig. 1).

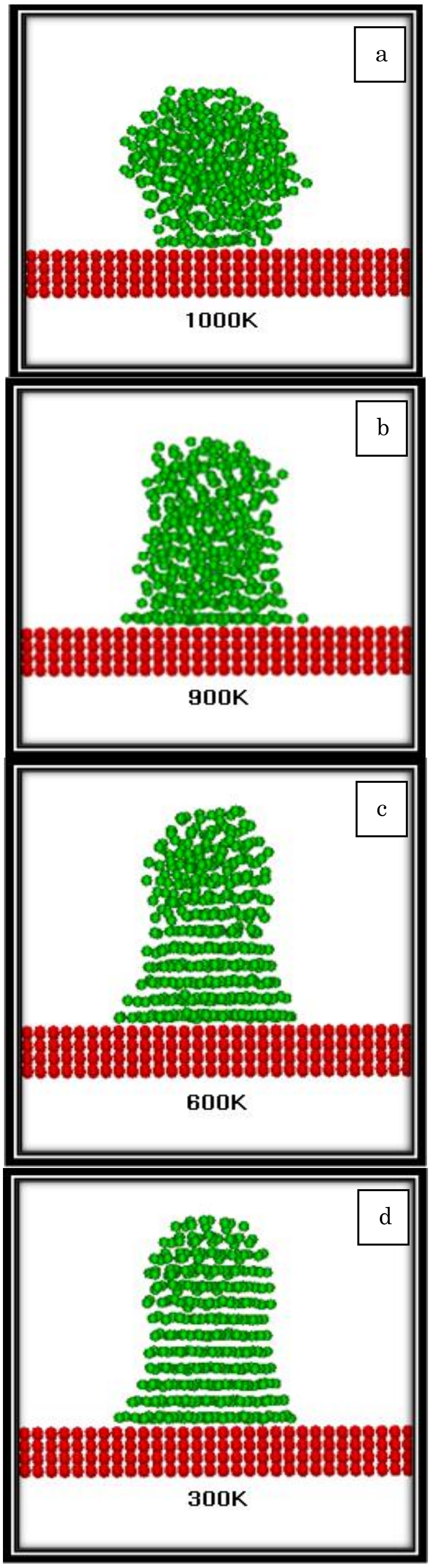

Fig. 1 – Side view of the contact angle for Ag nanodroplet at 1000 K, 900 K, 600 K and 300 K with 0.005 K/*fs* cooling rate

The temperature of nanodroplet decreased during spreading of nanodroplet on the Cu substrate. Figure 1 shows side view of Nanodroplet on the Cu substrate at 1000 K, 900 K, 600 K and 300 K. Fig. 1 shows recrystallization of nanodroplet at low temperature. The force behind this spreading is interatomic potential between Cu and Ag atoms. The periodic boundary condition was used in the X and Y axes and mirror boundary condition in the vertical to substrate i.e. Z axes. The wetting angles were determined from the side-view image of the nanodroplet.

In the melting process of nanodroplet the energy as well as order parameter are calculated in every time step. The phase transition is detected with use of diagram of energy or order parameter respect to temperature. The transition from the solid to the liquid phase can be identified by a jump in the energy diagram (Fig 2).

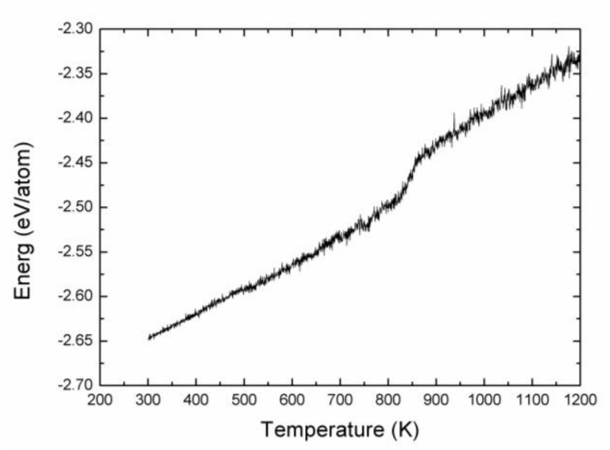

Fig. 2 – Variation of the energy of Ag nanodroplet with temperature

During the spreading of nanodroplet on the substrate, the cooling rate of nanodroplet was changed to investigate the effect of cooling rate on the contact angle. Our MD results for different cooling rate are listed in the Fig. 3. This figure shows to change contact angle with cooling rate of nanodroplet. The Contact angle varied from 41° to 73° with increasing cooling rate from 0.0001 to 0.01 K/fs. Wetability is optimized by minimizing the value of the contact angle, which corresponds to lower surface-interfacial energy. Therefore, the cooling rate is a parameter for wetability control in spreading process, which, is a very important issue in the reliability of electronic packaging.

The size dependence of the contact angle of Ag nanodroplet was also examined by varying the number of atoms in the nanodroplet. The other simulation parameters, including initial temperature, substrate, cooling rate, final temperature and time step value were same for all MD simulation. The pertinent results are displayed in Table 2. From this Table, we see that the contact angles for these three sizes of nanodroplet are approximately independence of size.

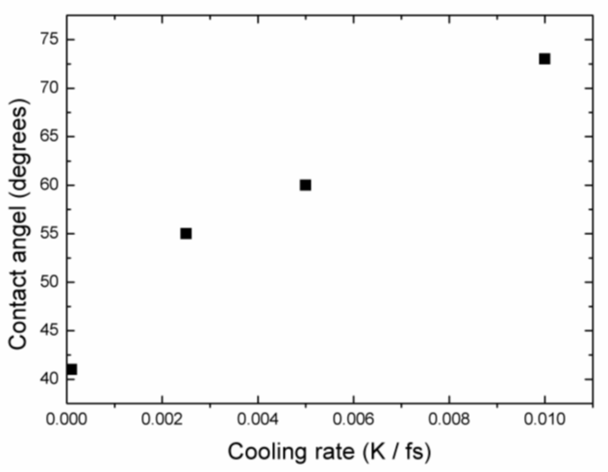

Fig. 3 – Contact angle of Ag nanodroplet on Cu substrate

Table 2 – Wetting angles of Ag nanodroplet as a function of number of atoms

No. of atoms	Temperature (K)	Contact angle
438	300	55
683	300	56
1058	300	54

Finally, the effect of initial temperature of nanodroplet on the contact angle was investigated by MD simulation. The cooling of nanodroplet started at 1000 K, 1150 K and 1300 K until the desired temperature. The other simulation parameters, including substrate, cooling rate, final temperature and time step value were same for all initial temperature. Table 3 shows the wetting angles as a function of initial temperature of nanodroplet. This table shows the contact angle decreased with increasing initial temperature. Therefore, initial temperature of nanodroplet is other parameter to control wetability in spreading process.

Table 3 – Wetting angles of Ag nanodroplet as a function of initial temperature

No. of atoms	Temperature(K)	Contact angle
438	1000	55
438	1150	46
438	1300	35

4. SUMMARY

The wetting angles of Ag nanodroplet on Cu substrate were obtained by molecular dynamics simulation technique. Increasing initial temperature reduced the contact angle, indicating good wetability. Also, our results show that decreasing cooling rate reduced the contact angle. Moreover, the contact angles of three size of Ag nanodroplet, including 438, 683 and 1058 atoms, were calculated on Copper substrate. The result show that contact angle is independent of the nanodroplet size approximately. In addition, a number of parameters such as cooling rate and temperature affect on the contact angle values. Therefore, we can optimize wetability of nanodroplet by control of a number of parameters.

REFERENCES

1. J.V. Geer, J.A.J. Hanraads, R.A. Lupton, J. Sci. *Commun.* **163**, 51 (2000).
2. S. Maruyama, T. Kimura, L.U. Ming-Chang, *Thermal Science & Engineering* **10**, 23 (2002).
3. J.A. Ko, H.J. Choi, M.-Y. Ha, S.D. Hong, H.S. Yoon, *Langmuir* **26**, 9728 (2010).
4. M.F. Arenas, V.L. Acoff, *J. Electronic Materials* **33** 1452 (2004).
5. P.T. Vianco, D.R. Fear, *JOM* **45**, 14 (1993).
6. H.K. Kim, H.K. Liou, K.N. Tu, *J. Mater. Res.* **10**, 497 (1995).
7. A.P. Xian, *Mater. Sci. Eng.* B **25**, 39 (1994).
8. H.H. Kart, M. Tomak, M. Uludoğan, T. Cagın, *Computational Materials Science* **32**, 107 (2005).
9. A.P. Sutton, J. Chen*, Phil. Mag. Lett.* **61**, 139 (1990).
10. H. Rafii-Tabar, A.P. Sutton, *Philosophical Magazine Letters* **63**, 217 (1991).
11. W.G. Hoover*, Phys. Rev.* A **31**, 1695(1985).
12. S. Nose, *J. Chem. Phys.* **81**, 511 (1984).
13. H.J.C. Berendsen, J.P.M. Postma, W.F. Van Gunsteren, A. Dinola, J.R. Haak, *J. Chem. Phys.* **81**, 3684 (1984).