

## 2.3 Microscopic Representation of Solid-Liquid-Vapor Interactions

The microscopic aspects of solid-liquid-vapor interactions are usually crucial when we consider theories of phase change phenomena such as nucleation of bubbles and droplets and the heat transfer at the three-phase interface. For a microscopic system, we need to start from the verification of the well-known Young-Laplace equation [eq. 2.2-?] and Young's equation [eq. 2.2-?] for the contact angle. In addition, for the reliable theory of the dropwise condensation, the determination of the condensation coefficient would be necessary. Furthermore, only by the thickness of a molecular mono-layer, the oxidation layer on the solid surface or the surfactant layer in the gas-liquid interface will drastically change the surface phenomena. In general, experimental assignments of such problems are usually extremely difficult since the scale is too small to access so the individual measurement of surface energy is almost impossible. Thus, in this section the molecular dynamics studies are discussed in order to understand such molecular scale phenomena.

**2.3.1 Molecular Dynamics Method and Force between Molecules.** Knowledge of statistical gas dynamics has been very helpful to understand the relationship between molecular motion and macroscopic gas dynamics phenomena. Recently, a direct simulation method using the Monte Carlo technique (DSMC) developed by Bird (1994) has been widely used for the practical simulations of rarefied gas dynamics. In the other extreme, statistical treatment of solid state matters has been well developed as the solid state physics [e.g. Kittel (1996)]. However, when we need to take care of liquid or inter-phase phenomena, which are inevitable for phase-change phenomena, neither gas-dynamics statistics nor the solid-state statistics are no longer valid at all.

The most powerful tool for the investigation of the microscopic phenomena of solid-liquid-vapor interaction is the molecular dynamics method [e.g. Allen and Tildesley (1987)], where the classical equations of motion (Newton's equations) are solved for a set of molecules.

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i = - \frac{\nabla \Phi}{\nabla \vec{r}_i}, \quad (2.3-1)$$

where  $m_i$ ,  $\vec{r}_i$ ,  $\vec{F}_i$  are mass, position vector, force vector of molecule  $i$ , respectively. For many kind of molecule systems, the potential  $\Phi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$  can be assumed to be the sum of effective pair potential  $\phi(r_{ij})$  as

$$\Phi = \sum_i \sum_{j>i} f(r_{ij}), \quad (2.3-2)$$

where  $r_{ij}$  is the distance of molecules  $i$  and  $j$ . Once the intermolecular potential is obtained, it is straightforward to numerically solve eq. (2.3-1). In principal, any of gas, liquid, solid states, and inter-phase phenomena can be solved without the knowledge of "thermo-physical properties" such as thermal conductivity, viscosity, latent heat, saturation temperature, and surface tension. It should be noticed, however, the validity of eq. (2.3-2) should be questioned when the density of molecules varies in a wide range.

An example of the pair potential is the well-known Lennard-Jones (12-6) potential expressed as

$$f(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (2.3-3)$$

where  $\epsilon$  and  $\sigma$  are energy and length scales, and  $r$  is the intermolecular distance as shown in Fig. 2.3-1. The intermolecular potential of inert monatomic molecules such as Ar and Xe are known to be reasonably expressed by this function. Moreover, many computational and theoretical studies are performed with this potential in order to investigate the general features of molecular dynamics. Here, the equation of motion can be non-dimensionalized by choosing  $\sigma$ ,  $\epsilon$  and  $m$  as length, energy and mass scale:  $r^* = r/\sigma$ ,  $t^* = t/\tau$  [ $\tau = \sigma(m/\epsilon)^{1/2}$ ],  $\phi^* = \phi/\epsilon$ , pressure  $p^* = p\sigma^3/\epsilon$ , number density  $N^* = N\sigma^3$ , density  $\rho^* = \sigma^3 \rho/m$ , temperature  $T^* = k_B T/\epsilon$ , where  $k_B$  is the Boltzmann constant. In order to illustrate the physical quantities, we can use the argon properties as  $\sigma = 3.4 \text{ \AA}$ ,  $\epsilon = 1.67 \times 10^{-21} \text{ J}$  ( $\cong 120\text{K}$ ),  $m = 40 \text{ amu}$ , and  $\tau = 2.2 \times 10^{-12} \text{ s}$ . Typical time step of the numerical integration of eq. [2.3-1]

is about  $0.005 \tau$  or 10 fs.

In order to simulate practical molecules, the determination of the potential function is very important. For example, many intermolecular potential functions have been proposed for water. The simple form of classical ST2 potential proposed by Stillinger and Rahman (1974) has still an advantage in computer task and in physical simplicity. The CC potential by Carravetta and Clementi (1984), that was constructed by fitting to the ab initio molecular orbital calculations has certainly better accuracy. Recently, SPC/E potential by Berendsen et al. (1987), which expressed the bending motion of HOH angle, is proved to have superior characteristics for liquid-vapor interface phenomena [Alejandre et al. (1995)].

**2.3.2 Liquid-Vapor Interface (Surface Tension and Young-Laplace Equation).** After solving the motion of each molecule, we need to average the molecular motion to obtain the macroscopic properties such as surface tension and condensation coefficient. Figure 2.3-2 shows examples of liquid-vapor interfaces of (a) liquid slab and (b) liquid droplet surrounded by its vapor [Maruyama et al. (1994a, 1994b)]. In both cases calculation region had periodic boundary conditions for all 6 boundaries. Starting from a crystal of argon continuing over side boundaries, the liquid slab with flat liquid-vapor interface in Figure 2.3-2 (a) was realized after 2 ns molecular dynamics simulation. Considering the periodic boundary conditions, this liquid slab can be regarded as an infinitely wide thin liquid film. During the simulation the number of molecules, volume and total energy of the system were conserved except for the early temperature control period. The vapor (white), interfacial (orange), and liquid (green) molecules are distinguished by the potential felt by each molecule. By taking a time average, the density profile (just counting the number of molecules in a finite volume), pressure tensor (calculating the virial function based on the statistical description), and surface tension can be reasonably predicted. The quite accurate prediction of surface tension have been demonstrated for Lennard-Jones fluid [Nijmeijer et al. (1988)] and water [Alejandre et al.

(1995)] by integrating the difference of normal  $p_N(z)$  and tangential  $p_T(z)$  components of pressure tensor across the surface as

$$\mathbf{s}_{lg} = \int_{z_l}^{z_g} [p_N(z) - p_T(z)] dz, \quad (2.3-4)$$

where  $z$  is the coordinate perpendicular to the interface. Here,  $p_N$  and  $p_T$  equals to the thermodynamic pressure  $p$  in bulk vapor position  $z_g$  or bulk liquid position  $z_l$ . In the case of liquid slab as shown in Fig. 2.3-2 (a), the integration between two vapor regions results in  $2\sigma_{lg}$  since there are two liquid-vapor interfaces.

On the other hand, the liquid droplet shown in Fig. 2.3-2 (b) was obtained when the initial argon crystal was placed at the center of the cubic region. This is regarded as an isolated liquid droplet floating in its vapor. For a liquid droplet, the Young-Laplace equation

$$\mathbf{s}_{lg} = \frac{(p_l - p_g)R_s}{2} \quad (2.3-5)$$

should be used to calculate the surface tension. We can obtain the pressure variation through liquid and vapor interface in order to obtain  $p_l$  and  $p_g$  as asymptotic values. However, the rigorous definition of the dividing radius  $R_s$  (which must be the surface of tension) is not straightforward, since the size of the droplet is normally very small and the liquid-vapor interface cannot be simply defined: see the interfacial molecules (orange) in Figure 2.3.2(b), which have different potential energy from liquid nor vapor. Detailed discussions about the estimation of surface tension of small liquid droplet can be found in the literatures [Thompson et al. (1984); Nijmeijer et al. (1992); Haye and Bruin (1994); Townsend and Rice (1991)]. Roughly a thousand molecules are enough to calculate the reasonable value of the bulk surface tension for argon [Maruyama et al. (1994a)].

**2.3.3 Condensation Coefficient.** The determination of the condensation coefficient by the molecular dynamics simulations is a very fascinating task as in the review of Tanasawa (1994). The condensation coefficient has been simply defined as the ratio of the condensation rate to the rate of

incident molecules to the interface. Through the detailed studies of the liquid-vapor inter-phase phenomena of argon, water, and methanol, Matsumoto et al. (1995b) and Matsumoto (1996) pointed out that this macroscopic concept cannot directly converted to the molecular scale concept. They stressed the importance of an ‘exchange’ process: a molecule condensed into the liquid phase let another liquid molecule to vaporize. By excluding those molecules from the number of condensing molecules, they had shown a good agreement with experiments. On the other hand, Tsuruta et al. (1996) had reported a significant dependence of the trapping rate on the normal velocity of incident molecules. They seek for the connection to the classical gas dynamics theory for the calculation of the condensation process. Since there are significant differences in these two approaches, probably, a new microscopic definition of the condensation coefficient may be necessary which is physically plausible and also useful for the further connection to the macroscopic theories.

**2.3.4 Solid-Liquid-Vapor Interactions (Contact Angle).** The contact phenomena of liquid to the solid surface are a critical issue of phase change heat transfer. The efficiency of the evaporation and condensation near the three-phase interface sometimes rules the macroscopic heat transfer rate. Figure 2.3-3 compares a snapshot of the liquid droplet in contact with a solid wall and a two-dimensional density distribution. Simulation conditions are similar to our previous report [Matsumoto et al. (1995a), Maruyama et al. (1998)], but 1944 argon molecules are included and about 1600 molecules constitute the liquid droplet (green) surrounded by the saturated vapor (orange). Solid molecules (blue) are located as three layers of fcc (111) surfaces with harmonic potential (only the surface layer is shown in Figure 2.3-3 for simplicity). The interaction potential between argon and solid molecule expressed by L-J potential is chosen so that the apparent contact angle becomes about  $90^\circ$ . Except for the 2 or 3 liquid layers near the surface, the averaged shape of the liquid droplet is close to the semi-spherical. In order to measure the contact angle, we can fit a circle to the density contour disregarding the 2 layers of liquid near the solid surface. The layered

structure is commonly observed for liquid-solid interfaces and explained as due to the solvation force [Israelachvili (1985)]. With stronger interaction potential, the spread of the first layer of liquid film is much more pronounced [Matsumoto et al. (1995a)]. Controversially enough, the cosine of measured contact angle or the average shape of the droplet far from the surface was linearly dependent on the strength of the surface potential.

There are good reviews of the connection between microscopic and macroscopic views of the wetting phenomena by Dussan (1979), and recently by Koplik and Banavar (1995). Saville (1977) has claimed that the Young's equation is not satisfied from his molecular dynamics results. He enclosed a liquid slab and coexisting vapor between two parallel surfaces represented by the one-dimensional potential function. Using 255 to 1205 L-J molecules at about the triplet temperature, he measured the meniscus of the liquid-vapor interface and compared with the calculated surface tensions  $\sigma_{lg}$  and  $\sigma_{sl} - \sigma_{sg}$ . However, Nijmeijer et al. (1990) showed a good agreement of the observed contact angle and the contact angle calculated from Young's equation. Sikken et al. (1988) and Nijmeijer et al. (1990) used a little different configurations with 8500 fluid molecules and 2904 solid molecules and the difficulty of the calculation of surface tension term  $\sigma_{sl} - \sigma_{sg}$  was also overcome. Later, Thompson et al. (1993) further supported the soundness of Young's equation and discussed even about the dynamic contact angle. Here, it should be noted that in addition to the accuracy of the calculation of surface energies, the definition of apparent contact angle has not been clear. It seems that the increase in number of molecules resulted the more attention to the bulk structure disregarding the few special layers. Anyway, the contact angle measurement by the molecular dynamics simulation as in Fig. 2.3-3 can be useful to predict the wettability of realistic molecules on a realistic surface [Fan and Cagin (1995)].

**2.3.5 Future Directions.** The sound understandings of molecular level phenomena are anticipated in varieties of phase-change theories such as nucleation of dropwise condensation, atomization,

homogeneous and heterogeneous nucleation of vapor bubbles in cavitation and boiling. Moreover, heat transfer right at the three-phase interface, which is a singular point in the macroscopic sense, should be considered for evaporation in micro-channel and for micro- and macro-layer of boiling. The upper limit of heat flux of phase-change must be clarified since recent advanced technologies such as intense laser light or electron beam easily achieve a very high heat flux. Phase change phenomena involved in thin film manufacturing process and laser manufacturing are often out of the range of the conventional approach. Other examples are surfactant effect in liquid-vapor interface and surface treatment effect of a solid surface.

Even though the molecular dynamics method is a powerful tool, the reader should notice its shortcomings that the spatial and temporal scale of the system which can be handled is usually too small to directly compare with the macroscopic phenomena. Even with the rapid advances of computer technology in a future, most of macroscopic problems cannot be handled by directly solving each motion of molecules. Then, the ensemble technique of the molecular motion and the treatment of boundary condition must be improved for the connection to macroscopic phenomena.

Moreover, the determination of potential function for molecules in real application is not straightforward and the assumption of classical potential fails when the effect of electrons is not confined in the potential form. For example, even a simple heat conduction in metal cannot be easily handled due to free electrons. Quantum feature of electrons must be considered when electrons are excited by laser light, by electromagnetic wave or by certain chemical reactions.

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## Nomenclature

$k_B$ : Boltzmann constant

$\vec{F}$ : force vector

m: mass

N: number density

p: pressure

R: radius

r: intermolecular distance

$\vec{r}$ : position vector

T: temperature

t: time

z: coordinate perpendicular to the interface

Green Symbols:

$\epsilon$ : energy parameter of Lennard-Jones potential

$\sigma$ : length parameter of Lennard-Jones potential

$\rho$ : density

$\Phi$ : potential

$\phi$ : pair potential

$\tau$ : time scale  $\tau = \sigma(m/\epsilon)^{1/2}$

Subscript:

g: gas

i: molecule index

l: liquid

lg: liquid-gas

N: normal direction

S: at surface of tension

sg: solid -gas

sl: solid-liquid

T: tangential direction

## Captions to Figures

Figure 2.3-1. Lennard-Jones potential.

Figure 2.3-2. Snapshots of argon liquid slab and droplet. White, orange and green represent vapor, interfacial, and liquid molecules, respectively. (a) Liquid slab and vapor made of 1944 molecules saturated at 100K in  $5.5 \times 5.5 \times 12$  nm box. (b) Liquid droplet and vapor made of 2048 molecules saturated at 95K in a 12 nm cubic box.

Figure 2.3-3. The molecular representation of a liquid droplet in contact with solid surface compared with the two-dimensional density profile. Orange, green and blue represent vapor, liquid and solid molecules, respectively. Higher density is denoted by red color in the density profile.