

How Can Molecular Simulations Contribute to Thermal Engineering? — Topics from Microbubbles and Microscale Heat Conduction —*

Mitsuhiro MATSUMOTO**

** Department of Mechanical Engineering and Science, Graduate School of Engineering, Kyoto University
Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan
E-mail: matsumoto@kues.kyoto-u.ac.jp

Abstract

This review covers several problems in thermal engineering which require consideration in nano-scale or at molecular level. One example in nanofluidics is “nano bubbles”; molecular simulation reveals that surface tension and vapor pressure of a spherical bubble hardly depend on its size and that the classical Young-Laplace equation is applicable even to a bubble as small as several nano meters. Combined with CFD schemes, molecular simulation can also treat oscillating dynamics of nanobubbles. Another example comes from solid-state physics, i.e., thermophysical properties of nano-scale elements. As the thickness of solid thin film decreases to “phonon mean free path”, the apparent thermal conductivity becomes smaller, the mechanism of which molecular simulation can explain.

Key words : Molecular Simulation, Microbubble, Nanofluidics, Thermophysical Properties, Thermal Conductivity

1. Introduction

Molecular simulation has become more and more popular in many fields of science and engineering since its birth in material physics in the 1950s. Owing to the development of computer hardware, we can now investigate a “huge” system consisting of 10^4 – 10^7 atoms, or trace a system for extremely long time, such as $1\ \mu\text{s}$.

We have to ask ourselves at this stage: With this powerful “tool”, what can/should we do in thermal engineering? What kind of contributions can the molecular simulation make to this field? The answers certainly vary. This review gives just a few but typical examples.

2. What is molecular simulation?

Molecular simulation can be classified from several viewpoints.

(1) To be based on classical (Newtonian) mechanics or to start from quantum mechanics: Various methods have been developed for the latter type, but there still exist severe restrictions on the system size. We focus on the classical mechanics simulation in this article.

(2) The main concern is either the analysis of static properties or the investigation of dynamic properties: Monte Carlo methods may be the best choice for the former purpose, but they cannot deal with dynamics in principle. There are a number of simulation methods for dynamics, such as molecular dynamics (MD), Brownian dynamics, and dissipative particle dynamics. DSMC (direct simulation Monte Carlo) is sometimes categorized also into this type. We pick up only MD simulations in this review.

2.1. Molecular dynamics method

The basics^{(1),(2)} are simple; we just trace all particles in the phase space, by numerically

solving the equations of motion. For that purpose, we have to assume appropriate interactions among particles, such as Coulombic force between ions, van der Waals interaction between neutral atoms, covalent bond, hydrogen bond, etc. As the model becomes more complex, the results are (in general) more realistic and reliable, but the required computer resources are sometimes desperately too much.

Once we choose a model, we can start the MD simulation from some appropriate initial conditions. After sufficient steps of integrating the equations of motion in terms of time, the system reaches an equilibrium state, and we can take the time average to investigate various static and dynamic properties. This is the equilibrium MD simulation; the first example (microbubble) in this article was based on this. We can also execute the time integration under some external forces, which is generally called a non-equilibrium MD (NEMD) simulation. Results of the second example (heat conduction in solid) were obtained with this type of simulation, where heat flux between two heat baths was investigated. It is convenient that data analysis in NEMD is done under a steady state because we can take time average. In the case of non-equilibrium and non-stationary simulations, the data analysis often becomes awfully laborious.

In the next two chapters, we describe why we need MD simulations and how we apply them, by taking problems in thermal engineering as examples.

3. Microbubbles

Microfluidics is a cutting edge of thermal and fluid engineering. As the system scale becomes smaller, new and interesting phenomena emerge. Among them are microbubbles, typical size of which is less than $100\mu\text{m}$. Recently various types of microbubble generators have been developed, and wide range of applications in MEMS, bioengineering, and environmental engineering have been proposed. However, there is a big puzzle about the mechanical stability of microbubbles.

3.1. Macroscopic Description

The starting point is the well-known Young-Laplace (Y-L) equation for a spherical bubble of radius R in equilibrium:

$$P_{vap} = P_{liq} + \frac{2\gamma}{R}, \quad (1)$$

where γ is the surface tension, P_{vap} and P_{liq} are the pressure inside and outside of the bubble, respectively. It is straightforward to derive Eq. (1) based on the principle of virtual work; the work δW required to change the radius from R to $R + \delta R$ is expressed as a sum of the volume change (δV) term and the area change (δA) term:

$$\begin{aligned} \delta W &= (-P_{vap} + P_{liq})\delta V + \gamma\delta A \\ &= (-P_{vap} + P_{liq})\delta \left[\frac{4\pi}{3}R^3 \right] + \gamma\delta [4\pi R^2] \\ &= 4\pi R^2 \left[(-P_{vap} + P_{liq}) + \frac{2\gamma}{R} \right] \delta R. \end{aligned} \quad (2)$$

The equilibrium condition is $\delta W = 0$, which leads to Eq. (1). The Y-L equation simply describes that the inside pressure is larger by $2\gamma/R$ than the surrounding pressure due to the surface tension.

3.2. What happens in microscale?

The problem is the term $2\gamma/R$ which diverges as $R \rightarrow 0$. Take water at room temperature as an example. The pressure difference $\Delta P \equiv 2\gamma/R$ is shown in Table 1, assuming $\gamma = 0.071\text{ N/m}$. When the bubble size is 1 mm – $100\mu\text{m}$, the pressure difference is negligible, or within the range of fluctuations. However, it becomes as large as 1 – 100 MPa for “nano bubbles”.

Table 1 Pressure difference ΔP of a spherical bubble in water at room temperature, based on Eq. (1).

Radius R	$\Delta P = 2\gamma/R$
1 mm	0.00014 MPa
1 μm	0.14 MPa
100 nm	1.4 MPa
10 nm	14 MPa
1 nm	140 MPa

There are two possibilities concerning the stability of microbubbles:

(1) The Y-L equation describes the macroscopic force balance, but does not hold at molecular scale.

(2) The Y-L equation holds also for nano bubbles, but the properties (γ and P_{vap}) are different from macroscopic ones.

It is extremely hard to experimentally investigate this point, but molecular simulation can.

3.3. Molecular simulation of a nano bubble

We carried out molecular dynamics simulation of a tiny bubble with various size⁽³⁾. The system consists of 25,000 or 125,000 particles, and the following simple Lennard-Jones (LJ) interaction potential is assumed among the particles:

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

where r is the distance between two particles, ϵ and σ are potential parameters. The phase diagram of the LJ fluid has been well investigated⁽⁴⁾. For example, the vapor-liquid critical temperature is $T_c^* = k_B T_c / \epsilon \simeq 1.32$ and the triple point temperature is $T_t^* = k_B T_t / \epsilon \simeq 0.67$. We chose two temperature conditions: $T^* = 0.7$, which is close to the triple point temperature, and a little higher one, $T^* = 1.0$. A cross-sectional view of a typical bubble is shown in Fig. 1. Assuming the size parameter $\sigma \simeq 0.3$ nm, the bubble radius is about 5 nm. We can generate a bubble with various sizes by changing the system volume. This is a "vapor" bubble; there are several particles evaporated from the bubble surface. However, the vapor density seems so low that we cannot expect the extremely high pressure predicted by the Y-L equation.

3.4. Pressure and surface tension

In molecular simulations, we can obtain the pressure with the virial expression:

$$P = \frac{N}{V} k_B T - \frac{1}{6V} \left\langle \sum_{i,j} \vec{r}_{ij} \cdot \frac{\partial \phi}{\partial \vec{r}_{ij}} \right\rangle, \quad (4)$$

where the first term on the right-hand side is the pressure of ideal gas, and the second term describes the "virial", or contribution of particle interactions.

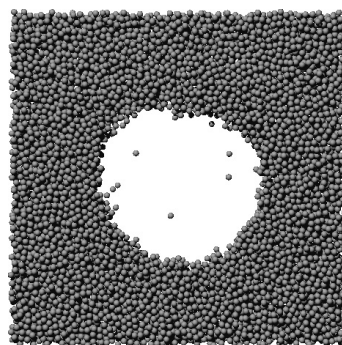


Fig. 1 Example of a nano bubble (sectional view) in Lennard-Jones liquid at $T^* = 0.7$.

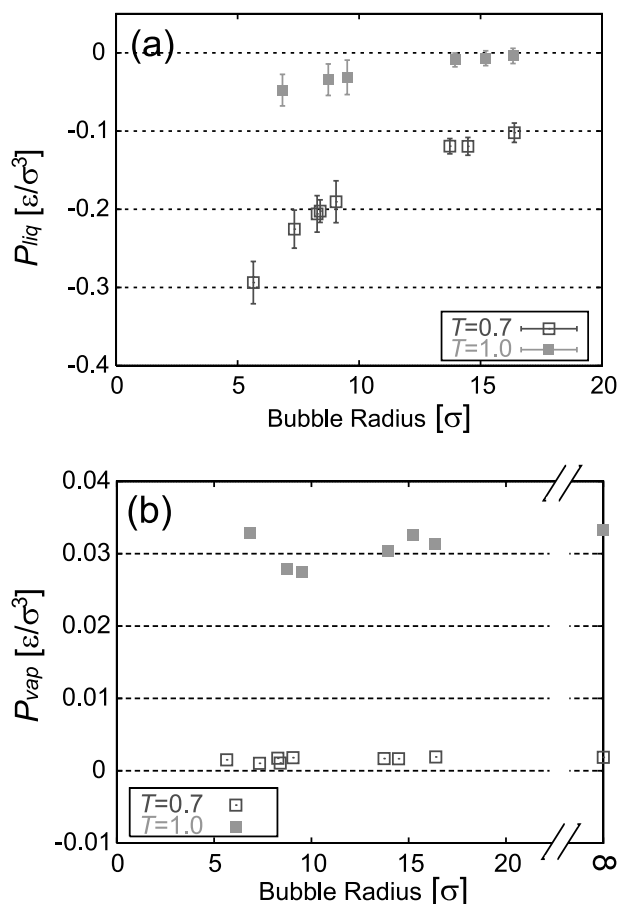


Fig. 2 Size dependence of the pressure of (a) liquid surrounding a bubble, and (b) vapor inside a bubble. The data at $R = \infty$ shows the saturated vapor pressure in bulk phase.

Applying Eq. (4) to particles in liquid region, the liquid pressure P_{liq} is obtained, as shown in Fig. 2(a). In general, P_{liq} takes negative values, which suggests that the surrounding liquid is in a “stretched state”. As the bubble size decreases, the liquid becomes more stretched.

The density of vapor inside the bubble is so low that Eq. (4) does not give reliable values of the vapor pressure P_{vap} . We estimated P_{vap} from the vapor density via an empirical equation of state. The results are shown in Fig. 2(b); it is amazing that the vapor pressure is independent of the bubble size.

There is a standard way to estimate surface tension in molecular simulations, i.e., spatial integration of stress tensor, similar to Eq. (4). This is well applicable to flat surface⁽⁵⁾, but calculation for curved surface is rather complicated⁽⁶⁾ and needs long time average. Instead, we evaluated γ from P_{vap} and P_{liq} , with assuming Eq. (1). The results are shown in Fig. 3; amazingly again, the surface tension is independent of the bubble size.

3.5. Validity of the Young-Laplace equation

Thus, molecular simulation reveals that

- (1) We can use the Y-L equation for a bubble as small as several nano meters.
- (2) The “parameters” appearing in the Y-L equation, i.e., P_{vap} and γ , are (almost) independent of the bubble size.

The above conclusion suggests that small bubbles can exist only in liquid under large negative pressure. Therefore, the microbubbles observed experimentally under atmospheric pressure should be either (i) at non-equilibrium state, (ii) containing non-condensable gas to

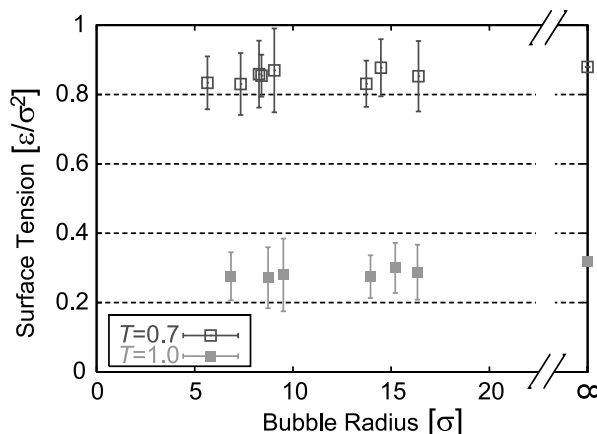


Fig. 3 Surface tension of a bubble.

support the surrounding pressure, or (iii) having contamination adsorbed on the surface to reduce the surface tension. Concerning (iii), it has been reported⁽⁷⁾ that microbubbles in water and aqueous solutions generally have negative charge (probably OH^- ions) on their surface. Such charge can drastically change the mechanical stability of microbubbles, and the details should be investigated at some molecular level, which will be a next target for molecular simulation.

3.6. Dynamics of microbubbles

Once the validity of the Y-L equation is established, we can investigate dynamics of microbubbles with continuum mechanics. For example, the Rayleigh-Plesset equation is reported to hold very well for a nano bubble⁽⁸⁾. However, problems remain for extremely rapid change of bubbles, such as bubble collapse during cavitation and sonoluminescence. Various assumptions about the basic continuum equations and the thermophysical properties are questionable.

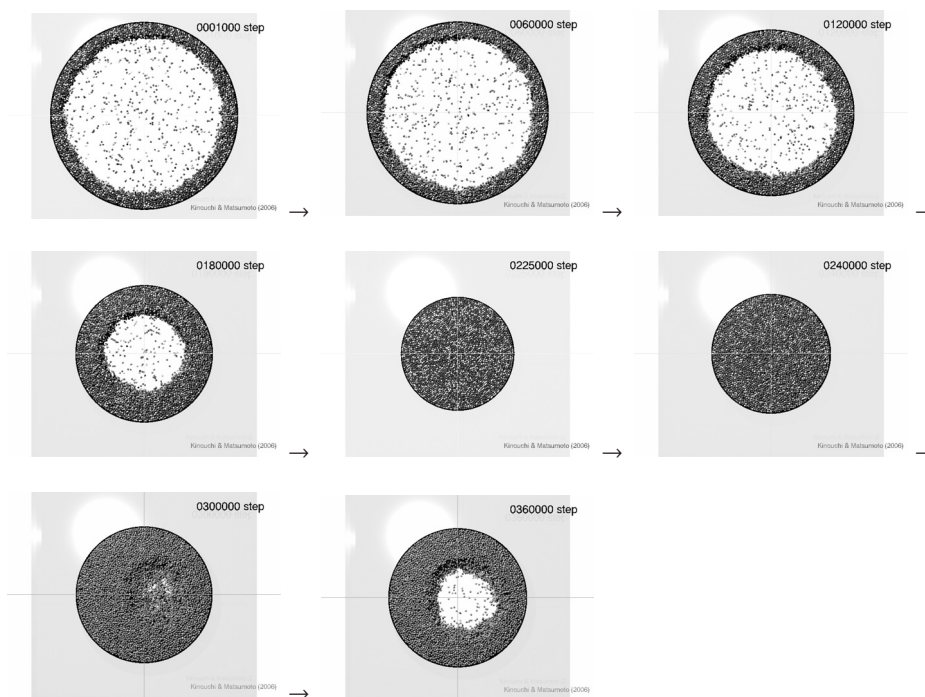


Fig. 4 Example of a hybrid simulation of spherical bubble collapse.

One of the solutions is a hybrid calculation, in which we focus on rapidly changing region by analyzing it with molecular simulation, and the remaining region is treated with conventional CFD. Examples are shown in Fig. 4, where spherical collapse and re-emergence of a bubble is shown under sudden pressure increase⁽⁹⁾. With this kind of hybrid simulation, we can investigate bubble dynamics without any assumptions about surface properties and phase change dynamics.

4. Heat conduction in solid device elements

Another example of contribution from molecular simulations is heat conduction in solid. Molecular simulation in material engineering and solid state physics often concerns microscopic structures, strength, or electronic properties, but heat transfer analysis of electronic devices is relevant in thermal engineering.

4.1. Continuum view of heat conduction

There are two types of carrier for energy transfer in solid; lattice vibrations (or “phonons” in quantum mechanics) and electrons. In semiconductor materials, both contributions are evenly important, which makes their thermal analysis complicated. Here, we limit the discussion to phonon analysis for simplicity.

Consider the situation that heat flux $\vec{q}$ is caused by a certain temperature gradient $\vec{\nabla}T$. In the linear regime, the Fourier law holds:

$$\vec{q} = -\lambda \vec{\nabla}T, \quad (5)$$

where λ is the thermal conductivity, which is a thermophysical constant for each bulk material. Analogy to the kinetic theory of gases relates λ to phonon properties⁽¹⁰⁾ as

$$\lambda \simeq \frac{1}{3}Cvl = \frac{1}{3}Cv^2\tau, \quad (6)$$

where C is the heat capacity of “phonon gas” per unit volume, v , l , and τ are the velocity (speed), the mean free path, and the relaxation time of phonons, respectively.

Here, l gives a characteristic length scale; in the case of crystalline silicon at room temperature⁽¹¹⁾, l is estimated to be 10–100 nm. It is interesting, and important in small-scale electronic devices, to see what happens when the system size decreases to be comparable to l . By analogy to photon radiation, Casimir⁽¹²⁾ reported in 1938 that, at extremely low temperature, l becomes macroscopic and the heat flux is solely determined by the temperature difference ΔT between both ends of the sample, not by the temperature gradient. As the scale of various solid devices reduces recently, this phenomenon reemerges.

4.2. Thought experiment

It is often said that the thermal conductivity of solid thin film is smaller than bulk value of the same material. There exist various experimental confirmations^{(11),(13)}. The ordinary explanation is that the phonon transport becomes “ballistic” in microscale, rather than “diffusive”. However, this explanation seems insufficient because ballistic transport itself should increase, not decrease, the energy flux.

Majumdar et al.^{(14),(15)} carried out a theoretical analysis based on a Boltzmann transport equation and concluded that, in the ballistic regime, the phonons are reflected at the sample boundaries, which causes the temperature jump there and reduces the heat flux. Figure 5 schematically depicts the change of temperature profile across the sample. However, the physical origin of the temperature jump is not fully understood and may depend on boundary conditions in solving the Boltzmann equation.

There is another possibility. Consider a solid film of thickness d under vertical temperature difference ΔT . In diffusive regime, the Fourier law predicts the heat flux as

$$q = \lambda \frac{\Delta T}{d}. \quad (7)$$

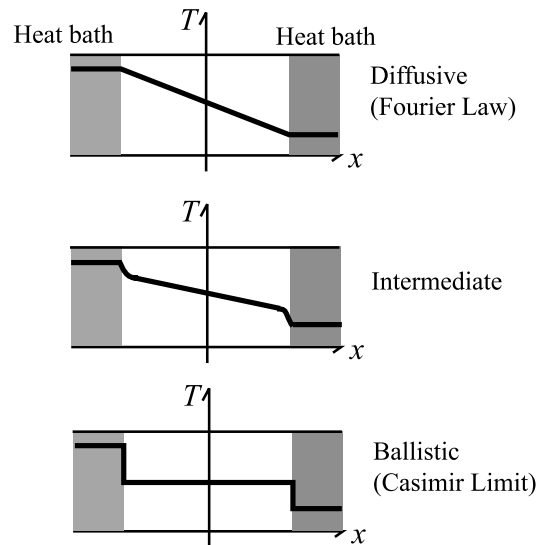


Fig. 5 Schematic temperature profile in steady state⁽¹⁴⁾.

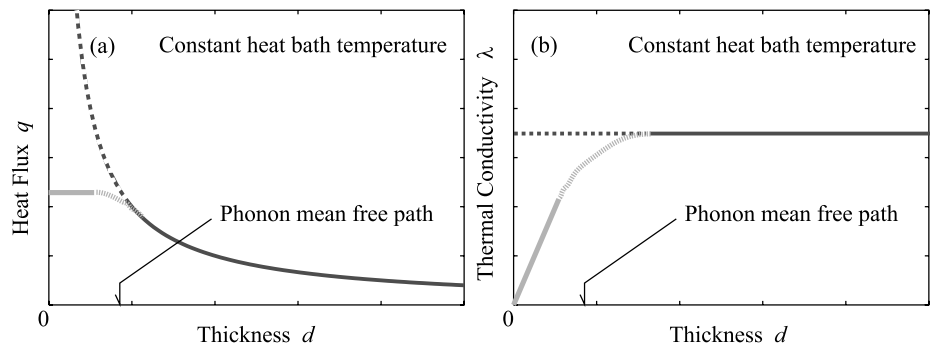


Fig. 6 Conjecture of thickness dependence of (a) heat flux and (b) apparent thermal conductivity of a solid thin film.

Now let d be reduced with keeping ΔT fixed. Equation (7) gives q diverging as d^{-1} . This is unphysical; q should approach a certain finite value, which corresponds to the Casimir limit, as shown in Fig. 6(a). The apparent thermal conductivity is defined as

$$\lambda = \frac{q \cdot d}{\Delta T}, \quad (8)$$

which is plotted in Fig. 6(b). Thus, the thermal conductivity of thin film decreases even if there is no temperature jumps at the boundaries. (We do not intend to negate the importance of the temperature jump; it should more or less exist at any boundaries.)

4.3. Molecular simulation of heat conduction

Many attempts have been reported on investigation of the solid thermal conductivity with MD simulations. The Kubo formula⁽²⁾, which calculates the autocorrelation of energy flux under equilibrium conditions, is applicable to estimate λ in bulk system. However, since we are interested in λ of finite system, the non-equilibrium (yet steady-state) MD simulation with heat baths on both ends is more feasible.

An example is an MD simulation of silicon “rod”, shown in Fig. 7; actually this is a “film” since we impose periodic boundary conditions except for the direction of heat flux. Heat baths are attached to both ends to control the spatially-averaged temperature at 300 ± 20 K with a simple velocity scaling technique. This kind of simulations require huge computational resources, partly because the system size is fairly large (the number of atoms is 60,000–

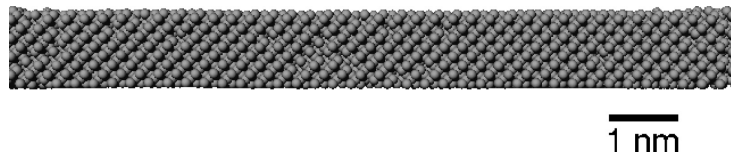


Fig. 7 A part of model silicon crystal for MD simulation.

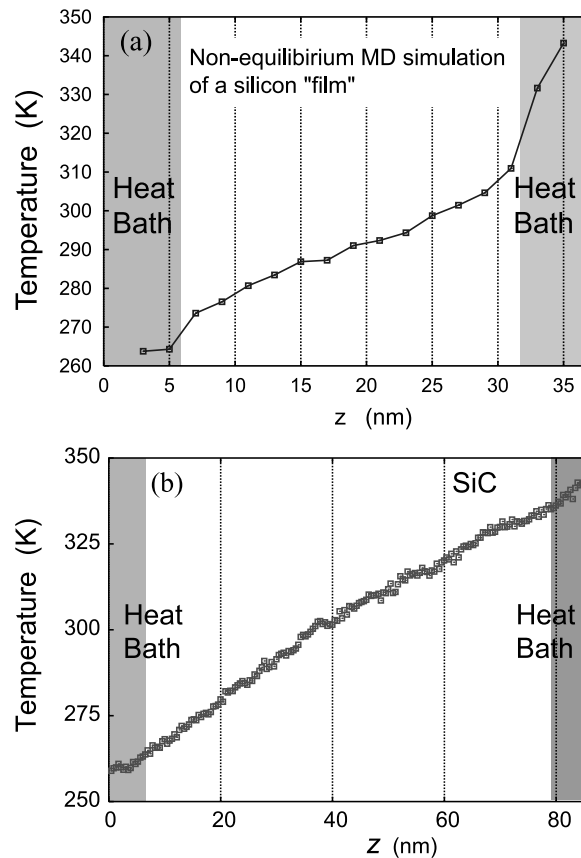


Fig. 8 Temperature profile across (a) silicon crystal and (b) SiC crystal.

100,000) and partly because long time average, typically for more than 1 ns, is needed to obtain values with high precision.

The typical temperature profile is depicted in Fig. 8(a), where large temperature jumps are clearly seen. However, we executed a similar MD simulation for silicon carbide (SiC) crystal, and found (almost) no temperature jumps, as shown in Fig. 8(b). We have not fully understood the reason yet. The temperature jump may depend on the technical detail of the "heat bath" temperature control. Comparison among various methods (velocity scaling, Nosé-Hoover, Langevin dynamics, etc.) would provide useful insights.

Since the LJ potential, Eq. (3), is much simpler than silicon or SiC potentials, model crystal consisting of LJ particles is an easier target to investigate. We have estimated the thickness dependence of the heat flux for a LJ thin film at $T^* = 0.4$. An example⁽¹⁶⁾ is shown in Fig. 9 as a logarithmic plot. As we expect, deviation from the Fourier law is clearly seen in the thin film regime.

4.4. Next steps

For the quantitative evaluation and modeling for thermal design of solid electronic devices, the following steps are indispensable:

- (1) Evaluation of energy transport in films: As described above, direct MD simulations

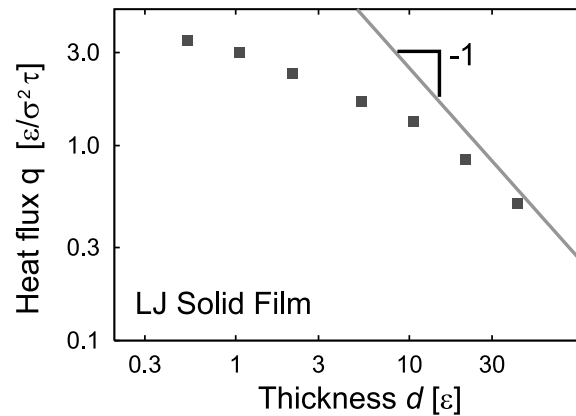


Fig. 9 Heat flux through Lennard-Jones crystal; the temperature of heat baths is fixed at $T^* = 0.4 \pm 0.01$.

in large scale are still required for further understanding of phonon transport dynamics. Different approaches^{(17),(18)} are also possible, such as estimation of phonon relaxation time which is necessary in Step (3).

(2) Evaluation of thermal resistance at boundaries: Several models, such as the acoustic mismatch model, were proposed, and comparisons with molecular simulation^{(19),(20)} have been reported.

(3) Phonon simulation at meso scale: Numerical analysis of the Boltzmann transport equation is the promising approach^{(21),(22)}, but the parameters should be determined either empirically, theoretically, or from MD simulations.

(4) Whole simulation of a device: The final goal is of course a whole simulation of devices or device elements, taking also account of electron transfer and electron-phonon interactions.

4.5. Other targets

One of the primary objectives of molecular simulation is to investigate materials, to which experimental access is very difficult. Material under extreme conditions (radioactive, at high pressure/temperature, etc.) is one example, and novel material is another.

Among the latters are quasi crystal (QC) solids, which locally have five- or ten-fold rotational symmetry but no global translational symmetry. Many QCs have been reported since the 1980s, but thermal properties in detail are not fully understood because large crystalline samples are difficult to obtain. We have developed a simple 2-dimensional model QC with modified LJ potential⁽²³⁾, as shown in Fig. 10, to investigate the lattice vibration properties. Compared with normal crystal, the QC is found to have much lower thermal conductivity,

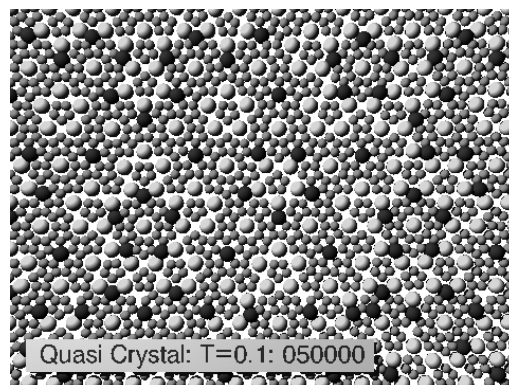


Fig. 10 Snapshot of a model quasi crystal.

although their lattice vibration structures resemble each other. This type of simulations can contribute much to develop or design novel materials.

5. Summary

Micro- and nano-scale systems are one of promising frontiers in thermal engineering. Giving two examples, nano bubbles in microfluidics and heat conduction in microscale solid elements, we showed that molecular simulation provides various opportunities for the research of these areas.

Acknowledgements

The author cordially thanks the collaborating students, K. Tanaka, S. Takamatsu, S. Kinouchi, N. Ikemoto, K. Fujiwara, M. Okano, T. Kunisawa, and S. Kawachi. A part of the work described here has been financially supported by Grant-in-Aid for Scientific Research from JSPS, and by The 21st Century COE Program for Research and Education on Complex Functional Mechanical Systems from Kyoto University.

References

- (1) Allen, M. P. and Tildesley, D. J., *Computer Simulation of Liquids*, Oxford University Press, 1989.
- (2) Frenkel, D. and Smit, B., *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press, 2001.
- (3) Matsumoto, M. and Tanaka, K., *Fluid Dynamics Research*, in press.
- (4) Hansen, J. P. and McDonald, I. R., *Theory of Simple Liquids*, 3rd ed., Academic Press, 2006.
- (5) Rowlinson, J. S. and Widom, B., *Molecular theory of capillarity*, Clarendon Press, 1982.
- (6) Ikeshoji, T. and Hafskjold, B., *Molecular Simulation*, **29** (2003) 101.
- (7) Takahashi, M., *J. Phys. Chem. B*, **109** (2005) 21858.
- (8) Okumura, H. and Ito, N., *Phys. Rev., E*, **57** (2003) 045301.
- (9) Matsumoto, M. and Kinouchi, S., *Proc. 2nd Int. Symp. Micro & Nano Technology* (Hsinchu, Taiwan, 2006) No. 63.
- (10) Kittel, C., *Introduction to Solid State Physics*, 8th ed., Wiley, 2004.
- (11) Tritt, T. M., *Thermal Conductivity: Theory, Properties, and Applications*, Kluwer Academic, 2005.
- (12) Casimir, H. B. G., *Physica*, **5** (1938) 495.
- (13) Valtz, S. (ed.), *Microscale and Nanoscale Heat Transfer*, Springer, 2007.
- (14) Majumdar, A., *J. Heat Trans.*, **115** (1993) 7.
- (15) Joshi, A. A. and Majumdar, A., *J. Appl. Phys.*, **74** (1993) 31.
- (16) Okano, M. and Matsumoto, M., in preparation.
- (17) McGaughey, A. J. H. and Kaviani, M., *Phys. Rev., B*, **69** (2004) 094303.
- (18) Matsumoto, M., Kunisawa, T., and Xiao, P., *J. Therm. Sci. Tech.*, **3** (2008) 159.
- (19) Matsumoto, M., Wakabayashi, H., and Makino, T., *Heat Trans. Asian Res.*, **34** (2005) 135.
- (20) Phillpot, S. R., Schelling, P. K., and Keblinski, P., *J. Materials Sci.*, **40** (2005) 3143.
- (21) Zeng, T. and Chen, G., *Trans. ASME: J. Heat Transf.*, **123** (2001) 341.
- (22) Yang, R., Chen, G., Laroche, M., and Taur, Y., *Trans. ASME: J. Heat Transf.*, **127** (2005) 298.
- (23) Matsumoto, M. and Kawachi, S., in preparation.