Expressions of the radius and the surface tension of surface of tension in terms of the pressure distribution for nanoscale liquid threads*

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The expressions of the radius and the surface tension of surface of tension R_s and γ_s in terms of the pressure distribution for nanoscale liquid threads are of great importance for molecular dynamics (MD) simulations of the interfacial phenomena of nanoscale fluids; these two basic expressions are derived in this paper. Although these expressions were derived first in the literature [Kim B G, Lee J S, Han M H, and Park S, 2006 *Nanoscale and Microscale Thermophysical Engineering*, **10**, 283] and used widely thereafter, the derivation is wrong both in logical structure and physical thought. In view of the importance of these basic expressions, the logic and physical mistakes appearing in that derivation are pointed out.

Keywords: nanoscale liquid thread, surface tension, surface of tension, pressure distribution

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1. Introduction

Molecular dynamics (MD) simulation is one of the useful methods to investigate the interfacial phenomena of nanoscale fluids, because it can provide detailed information on the molecular scale.[1,2] To use MD simulation to compute the radius and the surface tension of surface of tension R_s and γ_s is of great importance for the study of interfacial phenomena. To do this, the strict expressions of R_s and γ_s in terms of the pressure distribution are needed.[3,4] In a recent paper, Kim *et al.*[5] conducted MD simulations and presented a detailed characterization of the thermophysical properties of nanoscale liquid threads. As the basis of their MD simulations, they derived a couple of expressions of R_s and γ_s in terms of the pressure distribution for nanoscale liquid threads. However, this derivation is wrong both in logical structure and physical thought, although the results are correct. In this paper, a correct new derivation for these expressions will be given in Section 2 and the mistakes appearing in the previous derivation will be pointed out in the Appendix.

2. Derivation of the expressions of R_s and γ_s for nanoscale liquid threads

Consider the liquid thread of a liqud phase α surrounded by a vapor phase β. There must be a thin transition layer between phase α and phase β where the density of phase α changes to the density of phase β continuously. According to Gibbs, the physical system we are studying can be described by two bulk phases of constant densities of liqud and vapor, separated by a dividing surface of radius R located in the thin transition layer of the physical system, so R is not unique. For this model system, we have a general Laplace equation[3]

$$p^{\alpha} - p^{\beta} = \frac{\gamma}{R} + \left[\frac{\mathrm{d}\gamma}{\mathrm{d}R}\right], \tag{1}$$

where γ is the surface tension of the dividing surface and $[\mathrm{d}\gamma/\mathrm{d}R]$ is the derivative for the same physical state of the same system.

Neglecting the small difference between the two transverse components of the pressure tensor, the pressure tensor in cylindrical components is given by

$$\bar{\bar{P}} = p_{\mathrm{N}}(r)\,\boldsymbol{e}_{\mathrm{r}}\boldsymbol{e}_{\mathrm{r}} + p_{\mathrm{T}}(r)\,[\boldsymbol{e}_{\theta}\boldsymbol{e}_{\theta} + \boldsymbol{e}_{z}\boldsymbol{e}_{z}], \tag{2}$$

where $\boldsymbol{e}_{\mathrm{r}}$, $\boldsymbol{e}_{\theta}$ and $\boldsymbol{e}_{z}$ are orthogonal unit vectors, and $p_{\mathrm{N}}(r)$ and $p_{\mathrm{T}}(r)$ are the normal and transverse components of the pressure tensor respectively.[3] The mechanical equilibrium condition of pressure tensor $\nabla\cdot\bar{\bar{P}} = 0$ gives[5]

$$p_{\mathrm{T}}(r) = r\frac{\mathrm{d}p_{\mathrm{N}}(r)}{\mathrm{d}r} + p_{\mathrm{N}}(r). \tag{3}$$

Equation (3) gives

$$\frac{\mathrm{d}}{\mathrm{d}r}(r^2 p_{\mathrm{N}}(r)) = r(p_{\mathrm{N}}(r) + p_{\mathrm{T}}(r)). \tag{4}$$

Integrating Eq. (4), we obtain

$$(R^{\beta})^2 p^{\beta} - (R^{\alpha})^2 p^{\alpha} = \int_{R^{\alpha}}^{R^{\beta}} r[p_{\mathrm{N}}(r) + p_{\mathrm{T}}(r)]\,\mathrm{d}r, \tag{5}$$

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where R^α and R^β are the radii of two cylindrical surfaces inside the liquid and vapor, respectively, and p^α and p^β are pressures inside the liquid and vapor, respectively.

Besides, for the R satisfying $R^\beta > R > R^\alpha$, we have

$$\int_{R^\alpha}^{R^\beta} 2rp^{\alpha,\beta}(r,R)\,\mathrm{d}r = (R^\beta)^2 p^\beta - (R^\alpha)^2 p^\alpha + R^2(p^\alpha - p^\beta), \quad (6)$$

where $p^{\alpha,\beta}(r,R)$ is a defined function $p^{\alpha,\beta}(r,R) = p^\alpha\ (r < R)$, $p^{\alpha,\beta}(r,R) = p^\beta\ (r > R)$.

Combining Eqs. (5) and (6), we obtain

$$R^2(p^\alpha - p^\beta) = \int_{R^\alpha}^{R^\beta} r\mathrm{d}r[2p^{\alpha,\beta}(r,R) - p_\mathrm{N}(r) - p_\mathrm{T}(r)]. \quad (7)$$

Integrating Eq. (3) yields

$$\int_{R^\alpha}^{R^\beta} p_\mathrm{T}(r)\,\mathrm{d}r = R^\beta p^\beta - R^\alpha p^\alpha. \quad (8)$$

Substituting Eqs. (1) and (8) into

$$\int_{R^\alpha}^{R^\beta} p^{\alpha,\beta}(r,R)\,\mathrm{d}r = R^\beta p^\beta - R^\alpha p^\alpha + R(p^\alpha - p^\beta),$$

we obtain

$$p^\alpha - p^\beta = \frac{\gamma}{R} + \left[\frac{\mathrm{d}\gamma}{\mathrm{d}R}\right] = \frac{1}{R}\int_{R^\alpha}^{R^\beta} [p^{\alpha,\beta}(r,R) - p_\mathrm{T}(r)]\,\mathrm{d}r. \quad (9)$$

Equation (9) is a first-order ordinary differential equation for $\gamma(R)$. It can be written as

$$\begin{aligned} p^\alpha - p^\beta &= \frac{\gamma}{R} + \left[\frac{\mathrm{d}\gamma}{\mathrm{d}R}\right] = \frac{1}{R^2}\int_{R^\alpha}^{R^\beta} r[p^{\alpha,\beta}(r,R) - p_\mathrm{T}(r)]\,\mathrm{d}r \\ &\quad - \frac{1}{R^2}\int_{R^\alpha}^{R^\beta} (r-R)[p^{\alpha,\beta}(r,R) - p_\mathrm{T}(r)]\,\mathrm{d}r. \end{aligned} \quad (10)$$

We can prove that

$$\gamma = \frac{1}{R}\int_{R^\alpha}^{R^\beta} r\left[p^{\alpha,\beta}(r,R) - p_\mathrm{T}(r)\right]\mathrm{d}r \quad (11)$$

is a special solution of Eq. (10) as follows: from Eq. (11), we obtain

$$\begin{aligned} \left[\frac{\mathrm{d}\gamma}{\mathrm{d}R}\right] &= -\frac{1}{R^2}\int_{R^\alpha}^{R^\beta} r[p^{\alpha,\beta}(r,R) - p_\mathrm{T}(r)]\,\mathrm{d}r \\ &\quad + \frac{1}{R}\int_{R^\alpha}^{R^\beta} r\left[\frac{\mathrm{d}}{\mathrm{d}R}p^{\alpha,\beta}(r,R)\right]\mathrm{d}r \\ &= -\frac{1}{R^2}\int_{R^\alpha}^{R^\beta} r[p^{\alpha,\beta}(r,R) - p_\mathrm{T}(r)]\,\mathrm{d}r + (p^\alpha - p^\beta), \end{aligned}$$

which, combining with Eq. (9), gives

$$\left[\frac{\mathrm{d}\gamma}{\mathrm{d}R}\right] = -\frac{1}{R^2}\int_{R^\alpha}^{R^\beta} (r-R)[p^{\alpha,\beta}(r,R) - p_\mathrm{T}(r)]\,\mathrm{d}r.$$

Then we obtain Eq. (10).

So the general solution of Eq. (10) is

$$\gamma = \frac{1}{R}\int_{R^\alpha}^{R^\beta} r\left[p^{\alpha,\beta}(r,R) - p_\mathrm{T}(r)\right]\mathrm{d}r + \frac{C}{R}. \quad (12)$$

To determine the constant C, we consider the equivalence between the model system and the physical system. For the model system, the axial stress distribution is $p^{\alpha,\beta}(r,R) - \gamma(R)\delta(R-r)$ and the total axial stress of the model system must be equivalent to that of the real physical system, i.e.,

$$2\pi\int_{R^\alpha}^{R^\beta} r[p^{\alpha,\beta}(r,R) - \gamma(R)\delta(R-r)]\,\mathrm{d}r = 2\pi\int_{R^\alpha}^{R^\beta} rp_\mathrm{T}(r)\,\mathrm{d}r.$$

Substituting Eq. (12) into this equation gives $C = 0$. Thus the special solution equation (11) is the physical one.

Combining Eq. (7) and Eq. (11) gives

$$p^\alpha - p^\beta = \frac{\gamma}{R} + \frac{1}{R^2}\int_{R^\alpha}^{R^\beta} r[p^{\alpha,\beta}(r,R) - p_\mathrm{N}(r)]\,\mathrm{d}r. \quad (13)$$

Comparing Eq. (13) with Eq. (1) we obtain

$$\left[\frac{\mathrm{d}\gamma}{\mathrm{d}R}\right] = \frac{1}{R^2}\int_{R^\alpha}^{R^\beta} r[p^{\alpha,\beta}(r,R) - p_\mathrm{N}(r)]\,\mathrm{d}r. \quad (14)$$

The dividing surface with $R = R_\mathrm{s}$ satisfying

$$\left[\frac{\mathrm{d}\gamma}{\mathrm{d}R}\right]_{R=R_\mathrm{s}} = 0 \quad (15)$$

is called surface of tension.[3] The combination of Eqs. (14) and (15) gives

$$\int_{R^\alpha}^{R^\beta} rp^{\alpha,\beta}(r,R_\mathrm{s})\,\mathrm{d}r = \int_{R^\alpha}^{R^\beta} rp_\mathrm{N}(r)\,\mathrm{d}r. \quad (16)$$

From Eqs. (16) and (11), we obtain

$$\gamma_\mathrm{s} = \frac{1}{R_\mathrm{s}}\int_{R^\alpha}^{R^\beta} r[p_\mathrm{N}(r) - p_\mathrm{T}(r)]\,\mathrm{d}r. \quad (17)$$

From Eqs. (17) and (3), we obtain

$$\gamma_\mathrm{s} = -\frac{1}{R_\mathrm{s}}\int_{R^\alpha}^{R^\beta} r^2\frac{\mathrm{d}p_\mathrm{N}(r)}{\mathrm{d}r}\,\mathrm{d}r = -\frac{1}{R_\mathrm{s}}\int_0^\infty r^2\frac{\mathrm{d}p_\mathrm{N}(r)}{\mathrm{d}r}\,\mathrm{d}r, \quad (18)$$

from which, by using general Laplace Eq. (1) and Eq. (15), we obtain

$$R_\mathrm{s}^2 = -\frac{1}{p^\alpha - p^\beta}\int_0^\infty r^2\frac{\mathrm{d}p_\mathrm{N}(r)}{\mathrm{d}r}\,\mathrm{d}r \quad (19)$$

and

$$\gamma_\mathrm{s}^2 = -(p^\alpha - p^\beta)\int_0^\infty r^2\frac{\mathrm{d}p_\mathrm{N}(r)}{\mathrm{d}r}\,\mathrm{d}r. \quad (20)$$

3. Conclusion

A couple of expressions of the radius and the surface tension of surface of tension R_s and γ_s in terms of the pressure distribution for nanoscale liquid threads are derived. The logic and physical mistakes appearing in the derivation of the same expressions in Ref. [5] are pointed out.

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Appendix A

We pointed out the mistakes in the derivation of expressions of R_s and γ_s for nanoscale liquid threads in Ref. [5] in the following.

In Appendix A of Ref. [5], a liquid thread was considered. In cylindrical coordinates, the authors obtained the expression of the radius R_s, i.e., Eq. (A11) and that of the surface tension γ_s, i.e., Eq. (A12), which are the same as our Eq. (19) and Eq. (20), respectively. In Ref. [5], these two expressions were derived "by combining Eqs. (A1), (A3), (A7), and (A10) for $R = R_s$". Among these four Eqs., Eq. (A7) contains two equations, i.e., Eqs. (A7a) and (A7b)

$$p_N(r) = p^{\alpha,\beta}(r, R_s), \tag{A7a}$$

$$p_N(r) - p_T(r) = \gamma_s \delta(r - R_s), \tag{A7b}$$

where $\delta(r - R_s)$ is a Dirac's delta function.

In fact, it is wrong to make use of Eqs. (A7a) and (A7b) in the derivation of Eqs. (A11) and (A12). This is because Eqs. (A7a) and (A7b) are only a special singular solution of Eq. (A6) (i.e., our first order ordinary differential equation Eq. (9)) in Ref. [5] but not its complete solution, so that it is wrong to use this special singular solution to replace Eq. (A6) in the derivation of the expressions (A11) and (A12) containing continuous function $p_N(r)$. Based on such a derivation in Appendix A of Ref. [5], the expressions (A11) and (A12) (i.e., our Eqs. (19) and (20)) can only be looked at as two properties of the special singular solutions (A7a) and (A7b) and have nothing to do with continuous solution $p_N(r)$. This negates the validity of the derivation in Appendix A of Ref. [5].

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