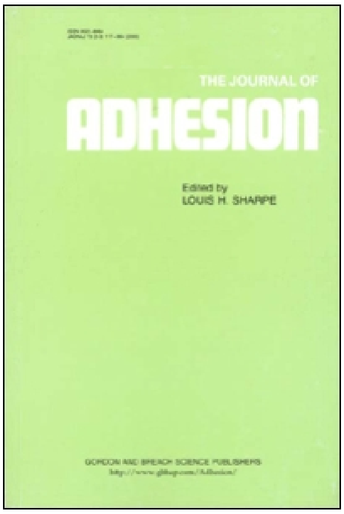

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Particle Adhesion to Drops

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The adhesion of spheroidal particles to spherical drops is calculated and discussed in terms of an equilibrium-penetration index. The present study emphasizes the case of particles that are sufficiently large to affect the drop volume upon penetration. It is shown that the more elongated the particles, the steeper the dependence of the penetration index on the contact angle. The effect of line tension on nanoscale particles is considered. Positive line tensions increase the steepness of the dependence of penetration index on contact angle whereas negative line tensions decrease this dependence. In addition, the energy barrier caused by positive line tensions is presented and discussed.

Keywords: Adhesion; Drop; Particle; Penetration; Wetting

INTRODUCTION

Particles adhere to liquid–fluid surfaces in a variety of situations [1–8]. The flotation of particles at such surfaces is essential for some separation processes [7] and is also used for characterization of particle wettability [6]. In addition, there is much (renewed) interest in particle-stabilized emulsions [2]. Thus, understanding the interaction

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of particles with liquid–fluid interfaces, specifically the adhesion of particles to drops, is of much interest.

The adhesion of particles to drops is a wetting phenomenon, which depends on many parameters. Among them, the shape and size of the particles play a key role in determining the extent of wetting. In most practical situations, the shape of the particles may be too complex to allow exact calculations. Therefore, spheroids have been used as model particles [1]. In addition, the size and shape of the particles determine the effect of line tension [1, 9]. Although the magnitude of line tension is still controversial, it seems to have become clear that it is in the range of 5×10^{-11} to 10^{-8} N. The effect of line tension on the contact angle is meaningful only for very small particles, usually less than 10^2–10^3 molecular distances [9]. Thus, recent interest in nanoparticles justifies the study of line-tension effects.

The objective of the present article is to discuss adhesion of particles to drops over a wide range of size and shape. For simplicity, prolate spheroids of various axis ratios are used for the calculations, with their axis of revolution parallel to the penetration direction. For particles that are large relative to the drops, the change in drop size because of the partial penetration of the particles has to be taken into account. For particles that are sufficiently small (mostly in the nanoscale range), line tension has to be considered. This article adds to recent studies [1] in treating relatively large particles, presenting the results in terms of a penetration index, and discussing the energy barrier caused by line tension.

THEORY

The system to be discussed is presented in Figure 1. It consists of a spherical liquid drop (L) of radius $\overline{R}$ and volume $\overline{V}$, and a solid particle (S) having a shape of an ellipsoid of revolution (spheroid) with axes $2\overline{a}$ and $2\overline{b}$ (axis of the revolution). The drop and the particle are surrounded by a fluid (F). For simplicity in the calculations, the particle is submerged in the drop in such a way that its axis of revolution is directed to the drop center. The extent of submergence is determined by the value of $\overline{\delta}$, which is the distance between the centers of the drop and particle. The distance between the drop center and the plane of intersection of the drop and the particle is $\overline{z}_i$. For convenience, the following dimensionless variables and parameters are introduced:

$$R \equiv \frac{\overline{R}}{\overline{b}},\ a \equiv \frac{\overline{a}}{\overline{b}},\ \delta \equiv \frac{\overline{\delta}}{\overline{b}},\ z_i \equiv \frac{\overline{z}_i}{\overline{b}},\ V \equiv \frac{\overline{V}}{\overline{b}^3}.$$

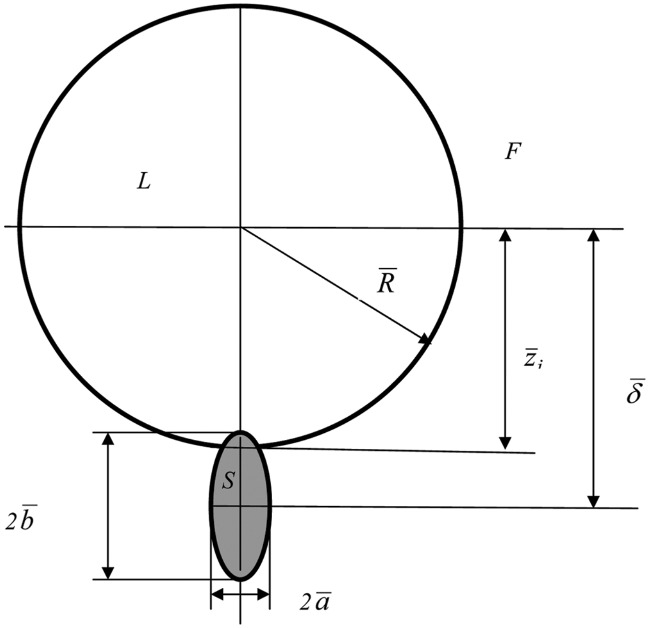

FIGURE 1 The particle-drop system.

The dimensionless Gibbs energy of the system, G, is given by

$$G \equiv \frac{\overline{G}}{\sigma_{\mathrm{LF}}\overline{b}^2} = -A_{\mathrm{SL}}\cos\theta + A_{\mathrm{LF}} + \tau L \tag{1}$$

where $\overline{G}$ is the Gibbs energy of the system, σ_{LF} is the liquid–fluid interfacial tension, θ is the contact angle that the solid makes with the liquid, $A_{\mathrm{LF}} \equiv \overline{A}_{\mathrm{LF}}/\overline{b}^2$, $A_{\mathrm{SL}} \equiv \overline{A}_{\mathrm{SL}}/\overline{b}^2$, $\overline{A}_{\mathrm{LF}}$ is the liquid–fluid interfacial area, and $\overline{A}_{\mathrm{SL}}$ is the solid–liquid interfacial area. The dimensionless line tension is defined by $\tau \equiv \overline{\tau}/(\overline{b}\sigma_{\mathrm{LF}})$, where $\overline{\tau}$ is the line tension and L is the dimensionless length of the contact line (normalized with respect to $\overline{b}$). The dimensionless interfacial areas are given by the following equations:

$$A_{\mathrm{LF}} = 4\pi R^2 - 2\pi R(R - z_i), \tag{2}$$

where

$$z_i = \frac{\sqrt{\delta^2 a^4 + (1-a^2)\left(R^2 + a^2\delta^2 - a^2\right)} - a^2\delta}{(1-a^2)} \quad \text{for } a \neq 1 \tag{3a}$$

$$z_i = \frac{R^2 + \delta^2 - 1}{2\delta} \quad \text{for } a = 1 \tag{3b}$$

$$A_{\mathrm{SL}} = \frac{\pi a}{\Delta}\left[\xi\sqrt{1-\xi^2} + \sin^{-1}\xi + \Delta\sqrt{1-\Delta^2} + \sin^{-1}\Delta\right] \quad \text{for } a \neq 1 \tag{4a}$$

where $\xi \equiv \Delta(z_i - \delta),\ \Delta = \sqrt{1-a^2}$, and

$$A_{\mathrm{SL}} = 2\pi(z_i - \delta + 1) \quad \text{for } a = 1. \tag{4b}$$

The equilibrium position of the particle is determined by minimizing the Gibbs energy of the system:

$$\frac{dG}{d\delta} = -\dot{A}_{\mathrm{SL}}\cos\theta + \dot{A}_{\mathrm{LF}} + \tau\dot{L} = 0 \tag{5}$$

where $\dot{A} \equiv dA/d\delta$ and $\dot{L} \equiv dL/d\delta$. Using Equations (2) and (4), one gets

$$\dot{A}_{\mathrm{SL}} = 2\pi a(\dot{z}_i - 1)\sqrt{1-\xi^2} \quad \text{for } a \neq 1, \tag{6a}$$

$$\dot{A}_{\mathrm{SL}} = 2\pi(\dot{z}_i - 1) \quad \text{for } a = 1, \tag{6b}$$

and

$$\dot{A}_{\mathrm{LF}} = 2\pi\left(2R\dot{R} + \dot{R}z_i + R\dot{z}_i\right). \tag{7}$$

The derivative of the dimensionless contact line in the case of the intersection between coaxial sphere and spheroid is given by

$$\dot{L} = 2\pi\frac{R\dot{R} - z_i\dot{z}_i}{\sqrt{R^2 - z_i^2}}. \tag{8}$$

Equation (5) is based on the assumption that line tension is constant for a given system. Actually, in contrast to surface tension, line tension is not a constant. It implicitly depends on the contact angle, and it also depends on the curvatures in the system [9, 10]. However, taking into account these effects makes the problem very complicated, especially if the particles are not spherical. Therefore, line tension is assumed here to be constant, and the results of the calculations should be considered an approximate indication.

The function $\dot{R} \equiv dR/d\delta$ may be derived from the condition of mass conservation of the liquid inside the drop, as follows:

$$V = \frac{4}{3}\pi R^3 - V_1 - V_2 = \text{const.} \tag{9}$$

Here

$$V_1 = \frac{\pi}{3}a^2\left[2 + 3(z_i - \delta) - (z_i - \delta)^3\right] \tag{10}$$

is the dimensionless volume of the submerged part of the particle (normalized with respect to $\overline{b}^3$), and

$$V_2 = \frac{\pi}{3}h^2(2R + z_i) \tag{11}$$

is the dimensionless volume of the "missing" spherical cap of the liquid (also normalized with respect to $\overline{b}^3$).

Using Equations (9)–(11), one gets

$$\dot{V} = 4\pi R^2\dot{R} - \dot{V}_1 - \dot{V}_2 = 0, \tag{12}$$

$$\dot{V}_1 = \pi a^2(\dot{z}_i - 1)\left[1 - (z_i - \delta)^2\right], \tag{13}$$

and

$$\dot{V}_2 = \pi(R - z_i)[2R\dot{R} - \dot{z}_i(R + z_i)]. \tag{14}$$

Differentiation of Equation (3) with respect to δ gives

$$\dot{z}_i = \frac{1}{(1 - a^2)}\left[\frac{a^4\delta + (1 - a^2)\left(R\dot{R} + a^2\delta\right)}{\sqrt{\delta^2a^4 + (1 - a^2)\left(R^2 + a^2\delta^2 - a^2\right)}} - a^2\right] \quad \text{for } a \neq 1 \tag{15a}$$

and

$$\dot{z}_i = \frac{2\delta R\dot{R} + \delta^2 - R^2 + 1}{2\delta^2} \quad \text{for } a = 1. \tag{15b}$$

There expressions may be represented in the form

$$\dot{z}_i = E_1\dot{R} + E_2, \tag{16}$$

where

$$E_1 = \frac{R}{\sqrt{\delta^2a^4 + (1 - a^2)\left(R^2 + a^2\delta^2 - a^2\right)}} \tag{17}$$

and

$$E_2 = \frac{a^2}{(1-a^2)}\left[\frac{\delta}{\sqrt{\delta^2 a^4 + (1-a^2)\left(R^2 + a^2\delta^2 - a^2\right)}} - 1\right] \quad \text{for } a \neq 1, \tag{18a}$$

$$E_2 = \frac{\delta^2 - R^2 + 1}{2\delta^2} \quad \text{for } a = 1. \tag{18b}$$

Equation (12) may now be represented in the following form:

$$F_1\dot{R} + F_2\dot{z}_i + F_3 = 0, \tag{19}$$

where

$$F_1 = 2R(R + z_i), \tag{20}$$

$$F_2 = -a^2\left[1 - (z_i - \delta)^2\right] + \left(R^2 - z_i^2\right), \tag{21}$$

and

$$F_3 = a^2\left[1 - (z_i - \delta)^2\right]. \tag{22}$$

Then, solving the system of Equations (16) and (19), one gets

$$\dot{R} = -\frac{F_3 + F_2E_2}{F_1 + F_2E_1}. \tag{23}$$

Integrating the system of ordinary differential equations (5) (left-side equality), (16), and (23), one gets the functions $R(\delta)$, $z_i(\delta)$, and $G(\delta)$. Then, the value of δ_m that provides the minimum in G according to Equation (5) may be found. Here and in the following, the subscript m corresponds to the equilibrium position.

A penetration index, p, which characterizes the equilibrium extent of penetration of a particle into the drop, may now be defined as

$$p = \frac{1}{2}(1 + R_m - \delta_m). \tag{24}$$

Obviously, $p = 0$ when the particle touches the drop and $p = 1$ when the particle fully penetrates into the drop.

RESULTS AND DISCUSSION

The minimum in Gibbs energy must correspond to the penetration index, for which the local contact angle is the ideal one [11]. In the absence of line tension, this would correspond to the state for which the local contact angle is the Young contact angle. In this case, these equations could have been simplified and numerical integration could have been avoided. However, when line tension is meaningful, its value and effect on the contact angle depend on the geometry of the contact line and the particle surface [11]. Then, numerical integration becomes unavoidable. Therefore, all the results in the present study have been attained by numerical integration. The Runge–Kutta method was used for the integrations.

Figure 2 demonstrates the effect of particle shape on the equilibrium-penetration index. It is clearly seen that as the particle becomes more elongated (a becomes smaller), the penetration index approaches a step function in its dependence on the contact angle. Thus, very long spheroids either almost completely penetrate into the liquid (for contact angles smaller than 90°) or almost completely remain in the fluid (for contact angles greater than 90°). This is in agreement with qualitative statements [8]. In contrast, the penetration index of spherical particles ($a = 1$) changes gradually with the contact angle.

As mentioned in the introduction, when the particles are sufficiently large compared with the drop size, their effect on the actual radius of the drop, for a given liquid volume, may not be negligible. This, in turn, may affect the penetration index. As shown in Figure 3, this is indeed the case, although the effect of the drop-to-particle-radius ratio, R, is not a major one. As can be seen, this effect practically disappears when $R > \sim 20$.

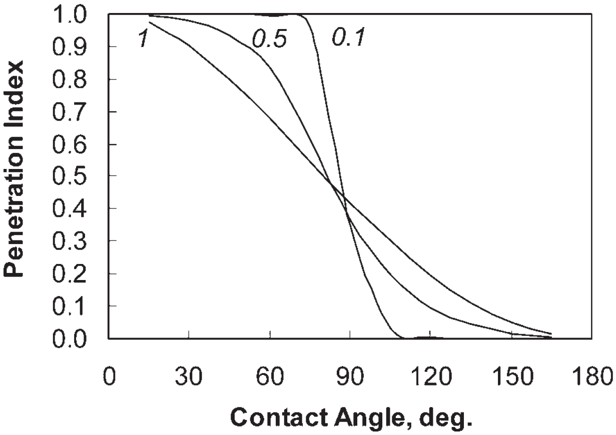

FIGURE 2 Attachment of a spheroidal particle to a spherical drop, assuming negligible line tension. Numbers near the curves indicate values of a.

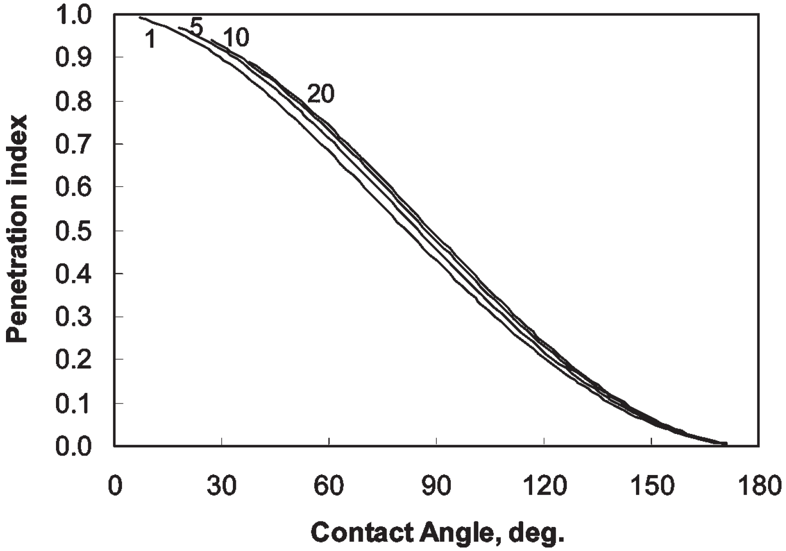

FIGURE 3 The effect of drop to particle radius ratio on the attachment of a spherical particle to a spherical drop. Numbers near the curves indicate the values of dimensionless drop radius, *R*.

Figures 4 and 5 demonstrate the effect of positive line tension on spherical and spheroidal particles, respectively. The value of line tension in these figures is given in its dimensionless form: $\tau \equiv \overline{\tau}/(\overline{b}\sigma_{\mathrm{LF}})$ [see definitions following Equation (1)]. To better understand the implications of the dimensionless line tensions used in these figures, it should be noted that a dimensionless line tension of 0.1 would correspond to $\overline{\tau} = 5 \times 10^{-11}\,\mathrm{N}$, $\sigma_{\mathrm{LF}} = 50\,\mathrm{mN/m}$, and $\overline{b} = 10\,\mathrm{nm}$. It should be noted that particles in this size range are prone to aggregation; however, only single particles are discussed in the present study. Aggregates may, in principle, be treated as larger particles with a more complex shape. As mentioned, the assumption of a constant line tension is a major simplification. However, the results may assist in understanding the qualitative effect. It is clearly seen that a positive line tension has the same effect as elongating the particles: the penetration index function become steeper as the value of line tension increases. In the case of spheroidal particles shown in Figure 5, positive line tension makes the penetration-index function very close to a step function. Figures 6 and 7 show the effect of negative line tension on spherical and spheroidal particles, respectively. It is clear that such values make the effect of the contact angle more gradual, even for spheroidal particles.

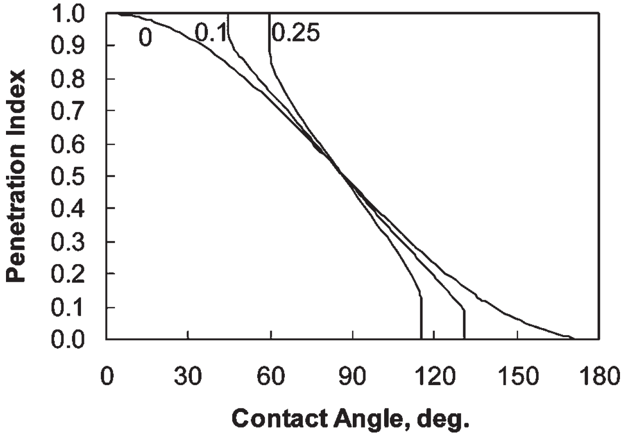

FIGURE 4 The effect of positive line tension on the attachment of a spherical particle to a spherical drop. $R = 10$, $a = 1$. Numbers near the curves indicate the values of the dimensionless line tension.

When line tension is negligible, the Gibbs energy of the system decreases as the particle penetrates the liquid–fluid interface on its way to equilibrium at the lowest energy. However, when line tension is meaningful in magnitude and positive, a maximum in the Gibbs energy, $\overline{G}_{\max}$, may exist. This is because the penetration of the particle

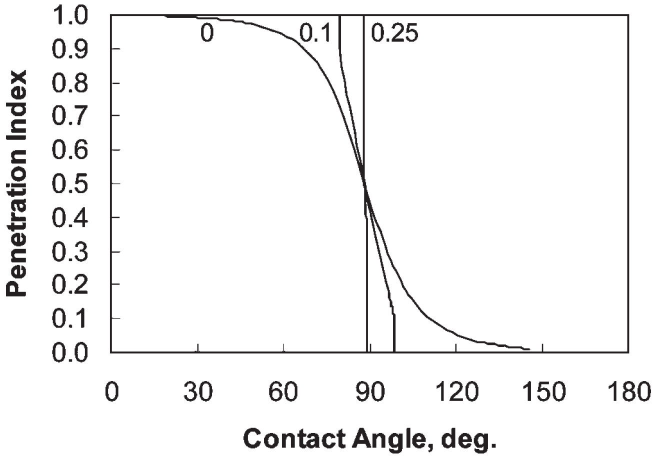

FIGURE 5 The effect of positive line tension on the attachment of a spheroidal particle to a spherical drop. $R = 10$, $a = 0.3$. Numbers near the curves indicate the values of the dimensionless line tension.

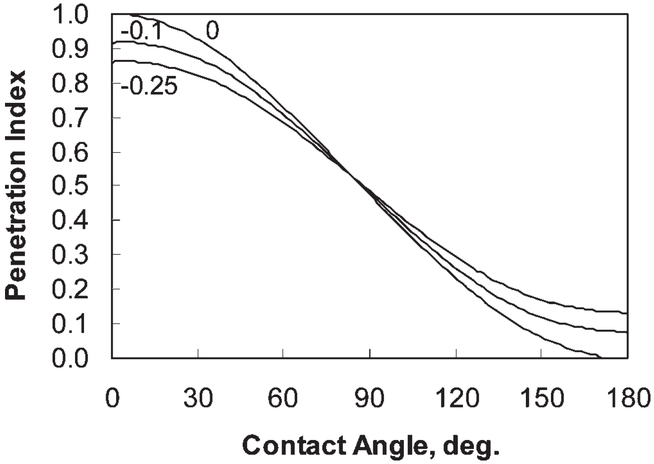

FIGURE 6 The effect of negative line tension on the attachment of a spherical particle to a spherical drop. $R = 10$, $a = 1$. Numbers near the curves indicate the values of the dimensionless line tension.

into the liquid–fluid interface increases, at first, the length of the contact line, thus increasing the energy associated with this line. The difference between $\overline{G}_{\max}$ and the Gibbs energy when the particle touches the drop is defined as the "energy barrier" for penetration,

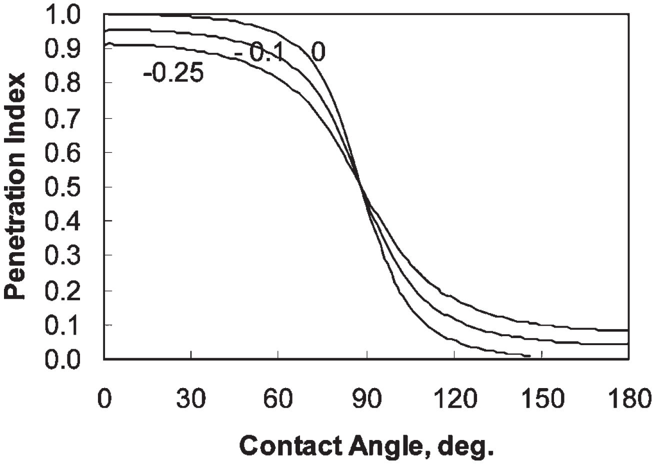

FIGURE 7 The effect of negative line tension on the attachment of a spheroidal particle to a spherical drop. $R = 10$, $a = 0.3$. Numbers near the curves indicate the values of the dimensionless line tension.

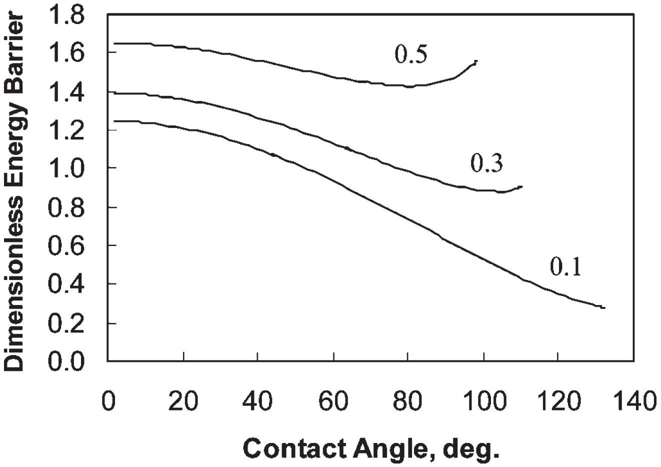

FIGURE 8 Dependence of the energy barrier (G_b) on the contact angle for a spherical particle. $R = 10$, $a = 1$. Numbers near the curves indicate the values of the dimensionless line tension.

$\overline{G}_b$. Figure 8 demonstrates the dependence of the dimensionless energy barrier, $G_b = \overline{G}_b/(\sigma_{\mathrm{LF}}\overline{b}^2)$ on the contact angle and on line tension for a spherical particle. The dimensionless line tension values used in this figure seem realistic for small particles of about 10 nm in size, as mentioned previously. In general, for contact angles that are not too high, the energy barrier tends to decrease with an increase in contact angle. The higher the line tension, the less sensitive is the energy barrier to the contact angle. To understand the practical implications of this energy barrier, it should be compared with the thermal energy of a particle, kT, where k is Boltzmann's constant (1.38×10^{-23} J/K) and T is the absolute temperature. At room temperature, for a particle size of 10 nm, $R = 10$, $\sigma_{\mathrm{LF}} = 72$ mN/m, $T = 293$ K, and $\theta = 90^\circ$, the energy barrier is of the order of (10^3kT). Thus, for nanoparticles, not only may the line tension be meaningful in determining the penetration index, but it may be important in determining a barrier for penetration.

CONCLUSIONS

The main conclusions of the present study can be summarized as follows:

1. The adhesion of particles to liquid drops can be quantified in terms of a penetration index, which refers to the equilibrium state of the

particle; it is defined as 0 when the particle touches the drop and 1 when the particle fully penetrates into the drop.

2. For the cases of prolate spheroidal particles, which are oriented with their axis of revolution parallel to the direction of penetration, the penetration index approaches a step function when the particle becomes very long and when the (positive) value of line tension is large.
3. A positive line tension may lead to a meaningful energy barrier that may prevent the penetration of particles into a drop, even when it is thermodynamically favored.

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