The influence of van der Waals forces on droplet morphological transitions and solvation forces in nanochannels

F Dutka\(^1\) and M Napiórkowski\(^2\)

\(^1\) Institute of Physical Chemistry, Polish Academy of Sciences, ulica Kasprzaka 44/52, 01-224 Warszawa, Poland
\(^2\) Institute of Theoretical Physics, Faculty of Physics, University of Warsaw, ulica Hoża 69, 00-681 Warszawa, Poland

E-mail: fdutka@ichf.edu.pl

Received 26 July 2013, in final form 24 October 2013
Published 28 November 2013

Abstract
The morphological phase transition between sessile and lenticular shapes of a droplet placed in a nanochannel is observed upon increasing the droplet volume. The phase diagram for this system is discussed within both macroscopic and mesoscopic approaches. On the mesoscopic level, the van der Waals forces are taken into account via the effective interface potential acting between the channel walls and the droplet. We discuss the contact angle dependence on the droplet volume and the distance between the walls; this angle turns out to be smaller than the macroscopic Young’s angle. The droplet’s presence induces the solvation force acting between the channel walls. It can be either attractive or repulsive, depending on the width of the channel.

(Some figures may appear in colour only in the online journal)

1. Introduction
The progress in miniaturization of microfluidic systems brings new challenges for the theoretical description of such systems. The behavior and manipulation of liquid droplets or gas bubbles (called the discrete phase) in a planar channel of micrometer size filled with an immiscible continuous phase is rather well understood [1–4]. In the absence of electrostatic interactions, and neglecting gravity (which plays a minor role on these scale), the droplet can be described by the macroscopic theory [5–7].

When the size of the channel becomes smaller and its height is below 100 nm, the droplet shape cannot be described by the macroscopic theory; one has to take into account the long-ranged van der Waals forces [8]. They give rise to an effective interaction between the walls of the channel and the droplet surface [9, 10]. In our mesoscopic description we consider droplets which do not touch the walls of the channel, and a thin layer of continuous phase separating the walls and the droplet is present [11]. This type of morphology will be investigated in the following analysis. The fabrication of nanochannels and filling them with liquid is already experimentally feasible [8, 12]; carbon nanotubes are good examples of such nanocapillaries [13–15]. Monte Carlo simulations have provided information on the influence of interparticle interactions on the structure of polymer solutions confined in nanopores [16].

The influence of the effective interface potential on the shape of the droplets in rectangular and circular capillaries has usually been investigated in two regions [9, 10, 17–22]. One region corresponds to the droplet surface close to the walls of the channel, where the disjoining pressure dominates. The second region corresponds to the droplet surface located in the center of the capillary, where the effect of disjoining pressure on the shape of the droplet can be ignored.

In our mesoscopic analysis we investigate channel heights in the range 10–100 nm and determine the influence of the effective interface potential on the droplet shape for any position of the droplet surface. We discuss in detail the geometry of the droplets, such as the thickness of the layer between the droplet and the walls of the channel, as well as the change of the apparent contact angle as a function of the increasing height of the channel.
Many of the previous papers on the shapes of droplets in microchannels have focused on droplets which were spread between the walls of the channel [23–26]. In the present analysis we put stress on the morphological transition between the sessile state (a droplet touching only one wall of the channel) and the lenticular state (a droplet touching both walls of the channel). The phase diagrams displaying this transition are presented and discussed, in section 2 for the macroscopic approach and in section 3 for the mesoscopic approach. In section 4, we point out the role of line tension when comparing the macroscopic and mesoscopic approaches. We also discuss the solvation force [27, 28] which emerges between the channel walls, in section 5. It turns out that in both macroscopic and mesoscopic approaches the sign of this force changes upon increasing the channel width, turning from repulsive to attractive. We show that the solvation force is zero in the situation when the droplet can be inscribed in a circle whose center coincides with the symmetry point of the droplet. Section 6 contains a discussion.

2. Macroscopic description

On the macroscopic level, one can distinguish three generic equilibrium shapes of a droplet of fluid A placed in a flat channel filled with fluid B; see figure 1. For simplicity, we consider a quasi-two-dimensional system which is translationally invariant in one direction. By the shape of the droplet we mean the shape of its cross section perpendicular to the direction in which the system is translationally invariant. Three different morphological states of the droplet can be characterized by the number of walls it remains in contact with: (0), the droplet does not touch any of the walls; (1), the droplet touches only one wall, and (2), the droplet touches both walls. In all three cases, the shape of the droplet can be described by an arc of a circle. In case (0), the droplet forms a full circle, and this state is called the circular state. In case (1), the shape is a circular segment, and we call this the sessile state. State (2) is called the lenticular (lens-shaped) state. Whenever the AB interface touches the wall, it forms with it an apparent contact angle \( \theta_y \). We note that generically by the contact angle one means the angle between the droplet interface and the wall, i.e., \( \pi - \theta_Y \). Here, we use the angle \( \theta_y \) to stress that one of the typical experimental realizations of such a system is the channel filled with liquid (the B-fluid), and its vapor represents the A-fluid. So, the angle \( \theta_Y \) is the angle formed by the droplet of liquid (B) deposited on a planar wall in ambient conditions (A). We shall often refer to Young’s equation:

\[
\cos \theta_y = \frac{\gamma_{AB} - \gamma_{AW}}{\gamma},
\]

where \( \gamma_{AB} \), \( \gamma_{AW} \), and \( \gamma \) are the wall–A fluid, wall–B fluid, and A-fluid–B-fluid surface tension coefficients, respectively. We consider angles \( 0 \leq \theta_y \leq \pi/2 \), which is the most common situation in droplet microfluidics [1, 2].

We assume that the fluids A and B are immiscible and incompressible such that the bulk free energy of the system with a droplet relative to the energy of the channel completely filled by phase B depends neither on the shape nor on the position of the droplet. It depends only on the cross-sectional area \( S \), which we shall often refer to as the droplet’s volume. To track the morphological phase transitions, we analyze only the surface free energies, which for the above three states are given by

\[
\begin{align*}
\Omega_0 &= 2\gamma \sqrt{\pi S}, \\
\Omega_1 &= 2\gamma \left( \pi - \theta_y + \sin \theta_y \cos \theta_y \right) \sqrt{S}, \\
\Omega_2 &= 2\gamma H \left( \frac{\pi - 2\theta_y}{2\cos \theta_y} + \sin \theta_y + \frac{1}{2} \cos \theta_y \frac{S}{H^2} \right). 
\end{align*}
\]

We notice that the energy of the circular state is always larger than the one corresponding to the sessile state: \( \Omega_0 = \Omega_1 \). There are thus two competing equilibrium states: sessile and lenticular. If, however, circular states are imposed on the system, e.g., via the constraint on the droplet to be placed symmetrically with respect to the center plane of the channel, then one also allows for the circular–lenticular transition.

For large enough volumes \( S \) the lenticular state has lowest surface energy; see figures 2 and 3. The equations \( \Omega_0 = \Omega_2 \) and \( \Omega_1 = \Omega_2 \) determine the coexistence curves. The circular, sessile, and lenticular states cease to exist for areas \( S_0 > S_{1}^{\text{max}} \), \( S_1 > S_1^{\text{max}} \), and \( S_2 < S_2^{\text{min}} \), respectively, which are given by

\[
\begin{align*}
S_{0}^{\text{max}} &= \frac{\pi H^2}{2}, \\
S_{1}^{\text{max}} &= \frac{4}{(1 + \cos \theta_y)^2} \left( \pi - \theta_y + \sin \theta_y \cos \theta_y \right), \\
S_{2}^{\text{min}} &= \frac{4}{(1 + \cos \theta_y)^2} \left( \pi - 2\theta_y \cos \theta_y - 2\tan \theta_y \right),
\end{align*}
\]

and determine the spinodal curves.

The free energy profiles corresponding to the circular–lenticular and the sessile–lenticular transitions are plotted as a function of \( S/H^2 \) for the special choice of \( \theta_y = \pi/4 \) in figures 3(a) and (b), respectively. In these figures the spinodal points are connected by the lines consisting of particularly constructed unstable states whose morphologies interpolate smoothly between the stable states. The free energies and volumes of these states are denoted by \( \Omega_0 \) and \( S_0 \) for the circular–lenticular transition, and \( \Omega_1 \) and \( S_1 \) for the sessile–lenticular transition. The unstable morphologies can be characterized by only one parameter, the contact angle \( \alpha \), which changes from \( 0 \leq \alpha \leq \theta_y \); see figure 3. For \( \alpha = \theta_y \), one has \( S_0 = S_0^{\text{min}} \) and \( S_1 = S_1^{\text{min}} \) (the lenticular state), while for \( \alpha = 0 \) the volume \( S_2 = S_2^{\text{max}} \) for the circular–lenticular transition, and \( S_1 = S_1^{\text{max}} \) for the sessile–lenticular transition.
Figure 2. The phase diagrams illustrating the circular–lenticular (a) and the sessile–lenticular (b) first-order transitions. The phase diagrams are plotted in the contact angle \( \theta_Y \) and the volume \( S \) variables. The solid lines denote the coexistence curves and the dashed lines are the spinodals. The surface energies \( (\Omega_0, \Omega_1, \Omega_2) \) and volumes \( (S_{0 \text{max}}, S_{1 \text{max}}, S_{2 \text{min}}) \) are given in (2) and (3), respectively.

The free energies of these particular unstable states are given by

\[
\Omega_{02} = 2\gamma H \frac{\pi - 2\alpha}{\cos \alpha}, \\
\Omega_{12} = 2\gamma H \frac{\pi - \theta_Y - \alpha + \cos \theta_Y (\sin \theta_Y - \sin \alpha)}{\cos \theta_Y + \cos \alpha}.
\]

(4)

One could think about other choices of unstable states, but these proposed here are characterized by only one parameter, and they smoothly interpolate between the spinodal points on figure 3. It turns out that such unstable states appear also in the mesoscopic description.

3. Mesoscopic description

3.1. Equilibrium shape of the droplet

In the mesoscopic description of droplet morphologies, we concentrate on configurations in which a layer of \( B \)-fluid phase always separates the \( A \)-fluid droplet from the wall. We assume the system to be translationally invariant in the \( y \)-direction, and due to the invariance of the confining walls in the \( x \)-direction the equilibrium shape of the droplet has to be symmetric with respect to the axis parallel to the \( z \)-axis. We fix this symmetry axis at \( x = 0 \) and place the walls of the channel at \( z = H \) and \( z = -H \) (figure 4). The shape of a droplet can be described by two functions, \( z = f(x) \) and \( z = -g(x) \), which connect smoothly at \( z = d \), with \( f'(x_d) = g'(x_d) = -\infty \). The parameter \( x_d \) is defined implicitly by the equation \( d = f(x_d) = -g(x_d) \). The constrained surface free energy of the droplet per unit length in the \( y \)-direction, often called the interface Hamiltonian, is

\[
\mathcal{H}[f, g] = \int_{-x_d}^{x_d} dx \left\{ \gamma \sqrt{1 + (f'(x))^2} + \omega (H - f(x)) - \omega (H + f(x)) + \gamma \sqrt{1 + (g'(x))^2} + \omega (H - g(x)) - \omega (H + g(x)) \right\},
\]

(5)

where \( \omega (\ell) \) is the effective interface potential between a flat wall and the interface at a distance \( \ell \) from it. The model of this potential stems from the microscopic density functional analysis for a one-component fluid in which the attractive parts of the fluid–fluid and wall–fluid interparticle pair potentials are given by [29–31]

\[
w(r) = -\frac{A_F}{(\sigma^2 + r^2)^3}, \quad w_W(r) = -\frac{A_W}{(\sigma_W^2 + r^2)^3},
\]

(6)
where \( A_F > 0 \) and \( A_W > 0 \) are the amplitudes of the interactions, while \( \sigma \) and \( \sigma_W \) are related to the molecular sizes of the fluid and wall particles; e.g., for argon \( \sigma \approx 0.3 \) nm [32]. For this model, the surface tension coefficient is given by [33]

\[
\gamma = \frac{A_F \pi}{8\sigma^2} (\rho_B - \rho_A)^2, \tag{7}
\]

and the effective interface potential is

\[
\omega(\ell) = \Delta \rho \frac{\pi}{4} \left[ \frac{\rho_B A_F}{\sigma^2} \tilde{\omega}(\ell/\sigma) - \frac{\sigma_W A_W}{\sigma_W} \tilde{\omega}(\ell/\sigma_W) \right], \tag{8}
\]

where

\[
\tilde{\omega}(\ell) = 1 - \ell \arctan \frac{1}{\ell}. \tag{9}
\]

Here, \( \Delta \rho = \rho_B - \rho_A \), and \( \rho_A, \rho_B, \) and \( \rho_W \) are the \( A \)-fluid, \( B \)-fluid, and wall densities, respectively. After introducing dimensionless quantities

\[
\hat{\rho} = \frac{1}{2} \left( 1 - \frac{\rho_A}{\rho_B} \right), \quad \hat{\lambda} = \frac{\rho_W A_W}{\rho_B A_F}, \quad \hat{\sigma_W} = \frac{\sigma_W}{\sigma}, \tag{10}
\]

the effective interface potential reduces to [33]

\[
\omega(\ell) = \gamma \left[ \hat{\omega} \left( \frac{\ell}{\hat{\sigma}} \right) - \frac{\hat{\lambda}}{\hat{\sigma_W}} \hat{\omega} \left( \frac{\ell}{\hat{\sigma_W}} \right) \right]. \tag{11}
\]

The surface tension coefficient and the effective interface potential in (7) and (8) can be also obtained from microscopic analysis of the two-component fluid at a planar wall for specific choice of parameters characterizing the interparticle interactions; see the appendix.

The macroscopic Young’s contact angle is given by

\[
\cos \theta_Y = 1 + \frac{\omega(\ell_\pi)}{\gamma}, \tag{12}
\]

where \( \omega(\ell_\pi) \) is the only minimum of the effective interface potential and \( \ell_\pi \) is the thickness of the adsorbed layer on a planar substrate. The effective interface potential \( \omega(\ell \to 0) \to \infty \), and \( \omega(\ell \to \infty) \to 0 \), so \( \omega'(\ell < \ell_\pi) < 0 \), and \( \omega'(\ell > \ell_\pi) > 0 \).

As the result of the minimization of the Hamiltonian under the constraint of the fixed volume \( S \) of the droplet,

\[
S = \int_{-x_d}^{x_d} dx \left( \tilde{f}(x) + \tilde{g}(x) \right) \tag{13}
\]

one obtains the following equations for the equilibrium shape of the droplet \( z = \tilde{f}(x) \) and \( z = -\tilde{g}(x) \):

\[
\begin{align*}
\frac{\tilde{f}''(x)}{(1 + \tilde{f}'(x))^2} &= -\tilde{\omega}'(H - \tilde{f}(x)) + \tilde{\omega}'(H + \tilde{f}(x)) - \lambda, \\
\frac{\tilde{g}''(x)}{(1 + \tilde{g}'(x))^2} &= -\tilde{\omega}'(H - \tilde{g}(x)) + \tilde{\omega}'(H + \tilde{g}(x)) - \lambda,
\end{align*} \tag{14}
\]

where \( \lambda \) is the Lagrange multiplier, and \( \tilde{\omega}(\ell) = \omega(\ell)/\gamma \). After one integration, we obtain

\[
\begin{align*}
\frac{1}{\sqrt{1 + \tilde{f}'(x)^2}} &= -\tilde{\omega}(H - \tilde{f}(x)) + \omega(H + \tilde{f}(x)) + \lambda \tilde{f}(x) + C_1, \\
\frac{1}{\sqrt{1 + \tilde{g}'(x)^2}} &= -\tilde{\omega}(H - \tilde{g}(x)) + \omega(H + \tilde{g}(x)) + \lambda \tilde{g}(x) + C_2.
\end{align*} \tag{15}
\]

The boundary conditions,

\[
\begin{align*}
\tilde{f}(x_d) &= -\tilde{g}(x_d) = d, \\
\tilde{f}'(x = 0) &= \tilde{g}'(x = 0) = 0, \\
\tilde{f}'(x_d) &= \tilde{g}'(x_d) = -\infty,
\end{align*} \tag{16}
\]

give

\[
\begin{align*}
\lambda &= \frac{f_0 \eta(f_0) + g_0 \eta(g_0)}{f_0 + g_0}, \\
C_1 &= -C_2 = \frac{f_0 g_0 (\eta(f_0) - \eta(g_0))}{f_0 + g_0}, \tag{17}
\end{align*}
\]

\[
\begin{align*}
d \eta(d) - 1 &= \lambda d + C_1,
\end{align*}
\]

where \( f_0 = \tilde{f}(x = 0), g_0 = \tilde{g}(x = 0) \), and \( \eta(z) = (1 + \omega(H - z) - \omega(H + z))/z \). In the case of a symmetric droplet, i.e., \( g_0 = f_0 \), the parameter \( \eta(f_0) \) becomes equal to the Lagrange multiplier.

Inserting the parameters \( \lambda, C_1, C_2, \) and \( d \) as a function of \( f_0 \) and \( g_0 \) into (15),

\[
\begin{align*}
\frac{1}{\sqrt{1 + \tilde{f}'(x)^2}} &= 1 - \tilde{f}'(x) \eta(\tilde{f}(x)) + \lambda \tilde{f}(x) + C_1, \\
\frac{1}{\sqrt{1 + \tilde{g}'(x)^2}} &= 1 - \tilde{g}'(x) \eta(\tilde{g}(x)) + \lambda \tilde{g}(x) + C_2,
\end{align*} \tag{18}
\]

one gets the equation

\[
\int_{d}^{f_0} \frac{d\tilde{f}'}{|\tilde{f}'(x)|} = \int_{d}^{g_0} \frac{d\tilde{g}'}{|\tilde{g}'(x)|} = x_d, \tag{19}
\]

which renders the values of \( g_0 = g_0(f_0) \). Thus the equilibrium shape of the asymmetric droplet for a fixed volume \( S \), (13), can be parameterized by one parameter, e.g., \( f_0 \), which is a function of the volume \( f_0 = f_0(S) \).
3.2. Symmetric droplet

Typical droplet shapes encountered in droplet microfluidics correspond to the lengths of the droplets, which are much larger then the channel height. Then the droplet is symmetric with respect to the plane parallel to the walls and located at the channel’s center [1, 2]. However, there are situations, for example in the flow-focusing method of droplet formation, in which the droplet is symmetrically deposited in channel and does not touch the sidewalls [1]. In this section, we discuss the shapes of such symmetric droplets. In particular, we investigate the dependence of the contact angle and the thickness of the films spanned between the walls and the droplet on the channel height.

For given macroscopic contact angle $\theta_y$, (1), and channel height $2H$, the volume $S$ determines the shape of the droplet. In the symmetric case one has $g_0 = f_0$, and (13) and (18) give the following relation:

$$ S = f_0^{3/2} \int_0^1 dt \frac{u(f_0, t)}{\sqrt{\eta(f_0) - \eta(f_0)}}. \quad (20) $$

where

$$ u(f_0, t) = \sqrt{1 - f_0^2 \frac{\eta(f_0) - \eta(f_0)}{1 - \eta(f_0)}}. \quad (21) $$

The function $u(f_0, t)$ is finite for $t \in [0, 1]$. The Lagrange multiplier $\eta(f_0)$ is positive for $f_0 > 0$ and has a minimum at $f_0 = f_m$, denoted as $\eta_m = \eta(f_0 = f_m)$; see figure 5. For $t \to 1$,

$$ \eta(f_0) - \eta(f_0) = -f_0 f_m^2 (1 - t) $$

$$ + \frac{1}{2} f_0 f_m^3 (1 - t)^2 + \cdots, \quad (22) $$

and it follows from (20) that $S \to \infty$ for $f_0 \to f_m$. Thus, for a given height of the channel, the minimal thickness of the film between the droplet and the wall $\ell_m = H - f_m$ is attained as $S \to \infty$. One can check that $\ell_m \leq R$, where $\ell_m$ fulfilling $o'(\ell_m) = 0$ is the thickness of the adsorption layer of the B-fluid on a planar substrate. For increasing $H$, the minimal film thickness behaves as

$$ \ell_m = \ell_x - \frac{\cos \theta_y}{\omega_0'(\ell_x)} \frac{1}{H^2} + O\left( \frac{1}{H^3} \right); \quad (23) $$

see figure 6.

Macroscopically, the apparent contact angle of the symmetric droplet in the lenticular state, see figure 1, is given by

$$ \cos \theta_y = \frac{H}{R}, \quad (24) $$

where $R$ is the radius of curvature of the droplet, and $H$ is at the same time one half of the channel height and the highest position of the droplet interface. In the mesoscopic description, we define the contact angle in the same way, and as the radius of curvature we take the inverse of the curvature at $z = 0$:

$$ \cos \theta = f_0 \left( \eta(f_0) + 2 \omega'(H) \right) $$

$$ = 1 + \omega(H - f_0) - \omega(H + f_0) + 2 \omega'(H) f_0. \quad (25) $$

Figure 5. The Lagrange multiplier $\eta(f_0)$ as a function of $f_0$ for $H = 100 \sigma$. The inset shows the close-up of $\eta(f_0)$ near its minimum at $f_0 = f_m$. The surface tension coefficient and the effective interface potential parameters are chosen such that $\theta = \pi/4$ and $\ell_x = 2 \sigma$. The effective interface potential $\omega(z) \propto 1/z^2$ for $z \gg 1$, so for large $H/\sigma$ and $S \to \infty$ the mesoscopic contact angle behaves as

$$ \cos \theta = 1 + \omega(\ell_m) - \omega(2H - \ell_m) + 2 \omega'(H)(H - \ell_m) $$

$$ = \cos \theta_y + \frac{\cos^2 \theta_y}{2 \omega_0'(\ell_x)} \frac{1}{H^2} $$

$$ - \omega(2H) + 2 \omega'(H) \frac{1}{H^3}. \quad (26) $$

The difference $\theta_y - \theta$ decreases with increasing height, and its relative value is smaller than 8 per mil already for $H = 50 \sigma$; see figure 7.

The confinement of the droplet puts a constraint on its curvature. As a result it cannot tend to zero for $S \to \infty$ as in the case of the sessile droplet deposited on a flat substrate [33]. Thus, provided that $\omega'(H) < 0$, it follows from (25) that the Lagrange multiplier $\eta(f_0)$ exhibits a global positive minimum for finite $H$; see figure 5. One deduces from (15) that the minimal film thickness $\ell_0 < \ell_x$, and thus $\theta < \theta_y$. 

![Figure 5](image-url)
Figure 7. The cosine of the mesoscopic contact angle $\theta$ (curve (a)) and its approximation (curve (b)), (26), as a function of $H$ for $S \to \infty$. The inset shows the relative difference between the contact angle of the droplet and the Young’s angle. The surface tension coefficient and the effective interface potential parameters are such that $\theta_Y = \pi/4$ and $\ell = 2\sigma$.

Figure 8. Surface energy $\Omega$ as a function of volume $S$ for symmetric (solid line) and asymmetric (dashed line) shapes for $\theta_Y = \pi/4$. The points $tr_{02}$, $tr_{12}$, $sp_0$, $sp_1$, and $sp_2$ denote the transition and spinodal points. The surface tension coefficient and the effective interface potential parameters are such that $\ell = 2\sigma$ and $H = 50\sigma$.

3.3. Morphological transition

The free energy $\Omega = \mathcal{H}[f, g]$ corresponds to the minimum of the constrained free energy $\mathcal{H}[f, g]$; see (5) and (14). Its dependence on the volume $S$ is displayed on figure 8. The points marked with $tr_{02}$, $tr_{12}$, $sp_0$, $sp_1$, and $sp_2$ denote the transition and spinodal points. The circular, sessile, and lenticular states cease to exist for points $(S_{sp0}, \Omega_{sp0})$, $(S_{sp1}, \Omega_{sp1})$, and $(S_{sp2}, \Omega_{sp2})$, respectively. The lines connecting the spinodal points correspond to unstable states. We notice that for $S > S_{sp1}$ droplets of asymmetric shapes cannot exist in a flat channel.

The droplet profiles fulfill (15) and can be parameterized by $f_0$ and $g_0$—the highest and lowest position of the interface; for symmetric droplets, $g_0 = f_0$. We recall that according to our assumption a layer of $B$-fluid is always present between the $A$-fluid droplet and the walls of the channel, so $f_0 < H$ and $g_0 < H$. For both the circular–lenticular and the sessile–lenticular transitions, the stable and metastable states are characterized by an increasing $f_0$ and $g_0$ as a function of $S$; see figure 9. We notice that as soon as the lenticular state is attained the parameter $f_0$ remains practically constant; it does not increase more than $0.1\sigma$; again, see figure 9. Upon increasing the volume of the droplets $S$ there is a jump in $f_0$ and $g_0$ at the transition points; see figure 10. In the circular state, the distance between the droplet surface and the wall is large enough such that the effective interaction between the wall and the droplet surface has practically no effect on the shape and the energy of the droplet. Thus we call this shape circular because its deviation from the circle is negligibly small. In mesoscopic analysis, the situation in which the droplet surface is within a distance $\ell = \ell_\pi$ to the
4. Line tension

We have already noticed that the mesoscopic circular states have practically the same energy as the macroscopic ones. On the other hand, the mesoscopic sessile and lenticular states have a lower free energy as compared to their macroscopic counterparts. The mesoscopic free energy, beside the contribution scaling with the surface of the droplet, contains also a line contribution connected with two (in the sessile state) and four (in the lenticular state) three-phase contact lines extending in the $y$-direction [34]. This line contribution was not taken into account in the macroscopic description. For long-ranged van der Waals forces rendering a continuous wetting transition and exploited in our analysis, the line tension coefficient is negative [35]. The formula for the line tension coefficient contains various contributions, among which the most significant one includes the interaction of the solid wall with the interface detaching from the wall. According to (4.4) in [35], it takes the form

$$\tau = \frac{1}{\tan \theta_Y} \int_{L_\pi}^\infty \omega(y),$$

and contributes roughly to one half of the value of the line tension coefficient. Although the authors in [35] analyzed the behavior of line tension in the vicinity of the wetting temperature, where $\theta_Y \to 0$, we use $2\tau$ as the estimate of the line contribution to the free energy stemming from a single three-phase contact line, also away from the wetting point.

The inclusion of the line tension into the macroscopic description results in a change of the value of the volume $S$ at which the morphological transitions take place. It can be calculated by solving the equations

$$0(S) = 2(S) + 8\tau,$$

$$1(S) + 4\tau = 2(S) + 8\tau$$

for the circular–lenticular and the sessile–lenticular transitions, respectively. In the case of the circular–lenticular transition, the values of $S_{tr}$ and $\ell_{tr}$ characterizing the morphological phase transition calculated within the mesoscopic description are well approximated by the values obtained within the macroscopic description with the inclusion of the line tension contributions; see figure 11. In the case of the sessile–lenticular transition this procedure leads to results presented in figure 12. The line tension calculated in the full mesoscopic description turns out to be smaller (more negative) than the approximate value $2\tau$ used within this simple approach.

The parameter $f_0$ characterizing the lenticular state, and therefore the contact angle $\theta$ (25), remains practically independent of the area $S$. For the values of the thermodynamic and geometric parameters considered in our analysis, and for $H > 50\sigma \approx 15$ nm, figure 7, the Young’s contact angle is a very good approximation of the mesoscopic contact angle. The relative difference is smaller than one per million. The line tension coefficient makes between 3% and 0.5% of the total free energy for $H$ within $50\sigma$–200$\sigma$. One could thus expect that the macroscopic description without
including the line tension contributions would predict the values of the volume at the phase transition to be located within a similar error margin, i.e., below 3%. However, this is not the case, and the difference between the macroscopic and mesoscopic descriptions is more pronounced, between 5% and 14%; see figure 13. The relative difference \( S_{\text{tr}}^{(M)}/S_{\text{tr}} - 1 \) between the volume at the circular–lenticular transition within the macroscopic description without including the line tension contributions \( (S_{\text{tr}}^{(M)}) \) and within the mesoscopic description \( (S_{\text{tr}}) \) decreases like \( 1/H \), as expected. In case of the sessile–lenticular transition the numerical results are less reliable, due to numerical errors induced by solving (19) and calculating the droplet shape and its free energy in the sessile state.

5. Solvation force

Insertion of an A-fluid droplet into a channel filled by B-fluid changes the free energy of the system and, in particular, modifies the solvation force acting between the sidewalls. The solvation force \( F \) is calculated as \( F = -\partial \Omega / \partial (2H) \) at fixed volume of the droplet.

In the macroscopic description, only the free energy of the lenticular state depends on the channel height, (2). The solvation force per unit length in the y-direction is thus non-zero, and is [25]

\[
F^{(M)} = -\frac{\partial \Omega_{\text{tr}}}{\partial (2H)} = \gamma \left( \frac{1}{2} \cos \theta_Y \frac{S}{H^2} - \frac{\pi - 2\theta_Y - \sin \theta_Y}{2} \right) = \frac{\gamma}{R} (2d - 2R \sin \theta_Y) = 2d \Delta p - 2\gamma \sin \theta_Y, \quad (29)
\]

where \( 2d \) is the length of the droplet–wall interface, \( R \) is the radius of curvature of the AB interface, and \( \Delta p = p_A - p_B = \)
For decreasing height and becomes negative for larger values; see figure 16.

In agreement with the macroscopic analysis conclusions, the lenticular state, \( \ell_0 \), the thickness of the film between the droplet and the wall, decreases and becomes zero when the arcs centers \( O_1 \) and \( O_2 \) merge on the symmetry axis, and becomes negative for larger values of \( H \); see figure 15. We notice that—for larger values of \( H \)—the lenticular state becomes metastable against the sessile or circular state. In particular, for large enough channel height, one has \( 2d = 0 \), and the lenticular state ceases to exist.

In the mesoscopic description, the free energy of the lenticular state, (5), is given by

\[
\mathcal{F}[\hat{f}] = 4 \int_0^{\hat{f}(x)} dx \left\{ \gamma \sqrt{1 + \left( \hat{f}'(x) \right)^2} + \omega(H - \hat{f}(x)) - \omega(H + \hat{f}(x)) \right\},
\]

where \( z = \hat{f}(x) \) describes the equilibrium shape of the droplet. Correspondingly, the solvation force is given by

\[
F = -\frac{\partial \mathcal{F}[\hat{f}]}{\partial (2H)} = -\frac{1}{2} \frac{\partial \mathcal{H}[\hat{f}]}{\partial H} = -2 \int_0^{\hat{f}(x)} dx \left\{ \omega'(H - \hat{f}(x)) - \omega'(H + \hat{f}(x)) \right\}.
\]

In agreement with the macroscopic analysis conclusions, the solvation force is positive for small values of the channel height and becomes negative for larger values; see figure 16. For decreasing \( H \), the thickness of the film between the droplet and the wall, \( \ell_0 = H - \hat{f}(x) \), decreases, and the derivative \( \omega'(\ell_0) \) becomes more negative; therefore the solvation force can be positive. For higher values of \( H \), the thickness \( \ell_0 \) increases, \( \omega'(\ell_0) \) becomes less negative, and the solvation force changes its sign.

The shape of the droplet corresponding to \( F = 0 \) is such that the radius of curvature \( R \) of the droplet at \( z = 0 \) equals \( x_d \); \( R = x_d \). In this situation, the \( A-B \) interface can be approximated by two arcs of the same circle with the center at \( (x = 0, \ z = 0) \); see figure 17.

6. Discussion

We have derived the phase diagrams for the circular–lenticular and the sessile–lenticular morphological transitions of a droplet in a channel within two approaches: macroscopic and mesoscopic. Since the free energy of the sessile state is always smaller than that of the circular state, the former transition can be observed only when droplet configurations which are symmetric with respect to the center plane of a channel are imposed on the system, for example via the appropriate constraint. Both morphological transitions are first-order transitions, and are accompanied by the presence of metastable and unstable states. In the mesoscopic description, the free energy profile, figure 8, is qualitatively the same as in the macroscopic description, figure 3. However, the...
macroscopic approach, which is not corrected by the inclusion of the line tension contributions, overestimates both the free energies and volumes at transition points by up to 14% as compared to the mesoscopic values; see figure 13. This comparison can be substantially improved by including the contact angle dependent line tension coefficient; see figures 11 and 12.

The long-ranged interparticle interactions taken into account in the analysis, (6), render the critical wetting transition at a planar substrate and lead to a negative line tension coefficient. The interparticle interactions leading to the first-order wetting transition give a positive line tension coefficient [36, 34]. We presume that in this case the values of volumes characterizing the sessile–lenticular transition would be larger than in the case of negative line tension coefficients. In addition to the modification of the transition points, also the spinodal points would change within the macroscopic description including the line tension contributions. Thus the analysis of the droplet states in the nanochannels might give us a hint about the underlying interparticle interaction and the order of the wetting transition.

In the mesoscopic description there is always a layer of the host B-fluid separating the A-fluid droplet from the channel walls. This is the most profound difference between the mesoscopic description and its macroscopic counterpart, where one allows for the droplet–wall interaction. Nevertheless, also in the mesoscopic approach one can define the contact angle \( \theta_z \); see (25). This angle approaches the macroscopic Young’s angle \( \theta_Y \) for \( H \to \infty \) and for droplet volume \( S \to \infty \). For mesoscopic channel heights and large droplets (\( S \to \infty \)), this angle is smaller than \( \theta_Y \); see figure 7. The difference \( \theta_Y - \theta \) decreases with increasing height, and its relative value is smaller than one per mil already for \( H = 50\sigma \).

In the mesoscopic description of the lenticular states of large droplets, the film thickness between the droplet and the wall \( \ell_0 = H - f_0 \) is smaller than \( \ell_x \), i.e., the thickness of the adsorption layer of the B-fluid on a planar substrate; see figure 6. The difference \( \ell_x - \ell_0 \) decreases with increasing channel height, and for \( H > 50\sigma \) it is smaller than 0.05\( \sigma \). Even this minor difference give rise to the positive (repulsive) solvation force. On the other hand, approximating \( \ell_0 \) by \( \ell_x \) would lead to the solvation force being always negative (attractive); see (31). This, in particular, would be incompatible with the macroscopic description where the force can change its sign.

The predicted change of sign of the solvation force in the lenticular state, also reported in [25, 24], brings a new issue into experimental microfluidics and nanofluidics. Suppose that one wall of the channel filled with the B-fluid can move in the direction perpendicular to it. Inserting many identical droplets of the A-fluid of fixed volume (with large enough distance between them to prevent their coalescence) will determine the distance between the walls of the channel. This height is a function of the number and the volume of the inserted droplets. Generally, droplets of A-fluid immersed in a channel filled with B-fluid can act as micродampeners or nanodampeners (shock absorbers).

**Acknowledgments**

FD was supported by Foundation for Polish Science within the project Homing Plus/2012-6/3, co-financed from the European Regional Development Fund. MN acknowledges support from the National Science Center via grant 2011/03/B/ST3/02638.

**Appendix. Effective interaction between a flat wall and a droplet surface**

Consider an interface fluctuating near a planar wall; see figure A.1. This interface separates the phases A and B rich in components 1 and 2, respectively. The thermodynamic state of the system corresponds to the coexistence of these A and B phases of the binary mixture. The system is invariant in the y-direction, and \( z = \tilde{f}(x) \) denotes the position of the interface. The interfacial Hamiltonian takes the form [37, 38]

\[
\mathcal{H}_{AB}[f] = \int_{-\infty}^{\infty} dx \left[ \gamma_{AB} \sqrt{1 + \left( \tilde{f}'(x) \right)^2} + \omega_{AB}(\tilde{f}(x)) \right],
\]

where \( \gamma_{AB} \) is the surface tension coefficient and \( \omega_{AB}(\ell) \) is the effective interface potential between the wall and the interface located at distance \( \ell \) from it. We consider the following model of long-ranged attractive interparticle \( W_{ij}(r) \) and wall–particle \( W_{iW}(r) \) interactions,

\[
W_{ij}(r) = -\frac{A_{ij}}{(\sigma_{ij}^2 + r^2)^{3/2}},
\]

\[
W_{iW}(r) = -\frac{A_{iW}}{(\sigma_{iW}^2 + r^2)^{3/2}},
\]

where \( i,j = 1,2 \) enumerate the fluid components. The amplitudes \( A_{ij} \) and \( A_{iW} \) are positive; the positive parameters \( \sigma_{ij} \) and \( \sigma_{iW} \) are related to the molecular sizes of the fluid.
and substrate particles. For this model, the surface tension coefficient is

\[
\gamma_{AB} = \frac{\pi}{8} \sum_{ij=1}^{2} \frac{A_{ij}(\rho_B - \rho_A)(\rho_B - \rho_A)}{\sigma_{ij}},
\]  

(A.3)

and the effective interface potential is

\[
\omega_{AB}(\ell) = \frac{\pi}{4} \sum_{ij=1}^{2} (\rho_B - \rho_A)
\left( \frac{A_{ij}}{\sigma_{ij}} \hat{\omega}(\ell/\sigma_{ij})
- \rho_W \sqrt{A_{WW}} \hat{\omega}(\ell/\sigma_W) \right),
\]  

(A.4)

where \(\rho_A\) and \(\rho_B\) denote the number density of \(i\)th component in phases A and B, \(\rho_W\) is the density of the wall, and

\[
\hat{\omega}(\ell) = 1 - \ell \arctan \frac{1}{\ell}.
\]  

(A.5)

For the following choice of the amplitudes and molecular sizes [39]

\[
A_{ij} = \sqrt{A_{ii}A_{jj}}, \quad A_{WW} = \sqrt{A_{ii}A_{jj}},
\]

\[
\sigma = \sigma_{ij}, \quad \sigma_W = \sigma_{WW},
\]

\(i, j = 1, 2,\)

the surface tension coefficient and the effective interface potential can be rewritten as

\[
\gamma_{AB} = \frac{\pi}{8\sigma^2} \left( \sum_{i=1}^{2} \sqrt{A_{ii}(\rho_B - \rho_A)} \right)^2,
\]  

(A.7)

\[
\omega_{AB}(\ell) = \frac{\pi}{4} \left( \sum_{i=1}^{2} \sqrt{A_{ii}(\rho_B - \rho_A)} \right)
\times \left( \sum_{j=1}^{2} \frac{\rho_B \sqrt{A_{jj}}}{\sigma^2} \hat{\omega}(\ell/\sigma)
- \rho_W \sqrt{A_{WW}} \hat{\omega}(\ell/\sigma_W) \right),
\]  

(A.8)

Upon introducing the dimensionless quantities

\[
\hat{\rho}_{AB} = \frac{1}{2} \left( 1 - \frac{\sum_{i=1}^{2} \sqrt{A_{ii}} \rho_A}{\sum_{i=1}^{2} \sqrt{A_{ii}} \rho_B} \right),
\]

\[
\hat{A}_{AB} = \frac{\rho_W \sqrt{A_{WW}}}{\sum_{i=1}^{2} \sqrt{A_{ii}} \rho_B},
\]

\[
\hat{\sigma}_W = \frac{\sigma_W}{\sigma},
\]

the effective interface potential reduces to

\[
\omega_{AB}(\ell) = \frac{\gamma_{AB}}{\rho_{AB}} \left[ \frac{\hat{\omega}(\ell/\sigma)}{\hat{\sigma}(\ell/\sigma_W)} - \frac{\hat{A}_{AB}}{\hat{\sigma}_W} \hat{\omega}(\ell/\sigma_W) \right],
\]  

(A.9)

which is exactly the form of the effective interface potential for the one-component system; see (11) and (61) in [33].

References

[1] Squires T and Quake S 2005 Rev. Mod. Phys. 77 977–1026
[2] Seemann R, Brinkmann M, Pföhl T and Herminghaus S 2012 Rep. Prog. Phys. 75 016601
[3] Jacobs K 2011 J. Phys.: Condens. Matter 23 180301
[4] Kadivar E, Herminghaus S and Brinkmann M 2013 J. Phys.: Condens. Matter 25 285102
[5] de Gennes P G, Brochard-Wyart F and Quere D 2004 Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves (London: Springer)
[6] Bonn D, Eggers J, Indekeu J, Meunier J and Rolley E 2009 Rev. Mod. Phys. 81 739–805
[7] Seemann R et al 2011 J. Phys.: Condens. Matter 23 184108
[8] Kim P, Kim H Y, Kim J K, Reiter G and Suh K Y 2009 Lab Chip 9 3255–60
[9] Hong H, Morris S and Radke C 1992 J. Colloid Interface Sci. 148 284–7
[10] Hong H, Morris S and Radke C 1992 J. Colloid Interface Sci. 148 317–36
[11] Ajaev V S 2012 Interfacial Fluid Mechanics: A Mathematical Modeling Approach (Berlin: Springer)
[12] Shui L, van den Berg A and Eijkel J C T 2011 Microfluid. Nanofluid. 11 87–92
[13] Megardis C M, Yaciziciglu A G, Libera J A and Gogotsi Y 2002 Phys. Fluids 14 L5–8
[14] Mattia D and Gogotsi Y 2008 Microfluid. Nanofluid. 5 289–305
[15] Bonthuis D J, Rinne K F, Falk K, Kaplan C N, Horinek D, Berker A N, Bocquet A and Netz R R 2011 J. Phys.: Condens. Matter 23 184110
[16] Chen H and Ruckenstein E 2009 Langmuir 25 12315–9
[17] Ajaev V S and Homsy G M 2001 J. Colloid Interface Sci. 240 259–71
[18] Ajaev V S and Homsy G M 2001 J. Colloid Interface Sci. 244 180–9
[19] Ajaev V S and Homsy G M 2006 Annu. Rev. Fluid Mech. 38 277–307
[20] van Honschoten J W, Brunets N and Tas N R 2010 Chem. Soc. Rev. 39 1096–114
[21] Starov V M 2010 Adv. Colloid Interface Sci. 161 139–52
[22] Mattia D, Starov V and Semenov S 2012 J. Colloid Interface Sci. 354 149–56
[23] Fortes M 1982 J. Colloid Interface Sci. 88 338–52
[24] Desouza E J, Brinkmann M, Mohrdieck C, Crosby A and Arzt E 2008 Langmuir 24 10161–8
[25] Kusumaatmaja H and Lipowsky R 2010 Langmuir 26 18734–41
[26] Broesch D J and Frechette J 2012 Langmuir 28 15548–54
[27] Butt H J and Kappl M 2009 Surface and Interfacial Forces (New York: Wiley)
[28] Dutka F and Napiórkowski M 2007 J. Phys.: Condens. Matter 19 466104
[29] Tasinkevych M and Dietrich S 2006 Phys. Rev. Lett. 97 106102
[30] Tasinkevych M and Dietrich S 2007 Eur. Phys. J. E 23 117
[31] Hofmann T, Tasinkevych M, Checco A, Dobisz E, Dietrich S and Ocko B 2010 Phys. Rev. Lett. 104 106102
[32] Hansen J P and Verlet L 1969 Phys. Rev. 184 151–61
[33] Dutka F, Napiórkowski M and Dietrich S 2012 J. Chem. Phys. 136 064702
[34] Schimmele L, Napiórkowski M and Dietrich S 2007 J. Chem. Phys. 127 164715
[35] Getta T and Dietrich S 1998 Phys. Rev. E 57 655
[36] Indekeu J 1992 Physica A 183 439–61
[37] Dietrich S and Napiórkowski M 1991 Phys. Rev. A 43 1861–85
[38] Hiester T, Dietrich S and Mecke K 2006 J. Chem. Phys. 125 184701
[39] Dutka F, Napiórkowski M and Dietrich S 2008 Phys. Rev. E 78 021602