

## Bulge test at nano-scale: The surface effects

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Bulge test is an effective technique to measure the mechanical properties of thin films. As the membrane size decreases to nano-scale, the surface effect plays a significant role in determining the mechanical behavior of the membrane, and the techniques commonly used to measure the bulk materials properties are not applicable. We explore the surface effect on the nano-scale bulge test using combined continuum theories and atomistic simulations. We formulate the load-deflection relation by incorporating the surface effect and analyze its size-dependent behavior. The present theoretical model is in quantitative agreement with the molecular dynamics simulations. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4817298>]

The mechanical properties of nano-scale structures can be measured by various techniques such as the microtensile test,<sup>1</sup> nano-indentation,<sup>2,3</sup> and the bulge test.<sup>4,5</sup> A new setup of bulge test has been developed recently which incorporates an atomic force microscope (AFM).<sup>6</sup> It allows an *in situ* recording of topographic images of the samples under different load conditions. The improvement on resolution renders this technique particularly suitable for the nano-scale measurements.

Bulge test has been performed to measure the mechanical properties of a number of nano-scale membranes such as freely suspended nanocomposites,<sup>7</sup> free-standing hybrid nanofilms,<sup>8</sup> circular cross-linked polymeric membranes,<sup>9</sup> and one-nanometer rectangular carbon nano-sheets.<sup>10</sup> In the above examples, the load-deflection relation derived for the bulk materials is used to extract the elastic modulus of the nano-structures. However, it is noteworthy that as the material size decreases to nanometers, the surface effects become prominent in determining its mechanical behavior.<sup>11–15</sup> Such effects usually result in the size-dependent performance of the nano-structures which is largely deviated from the bulk materials behavior. In this letter, we explore the surface effects on the nano-scale bulge test using combined continuum theories and atomistic simulations. We refine the load-deflection relation by incorporating the surface effects and analyze its size-dependent nature. We further employ molecular dynamics (MD) simulations to obtain the material parameters of a nano-scale aluminum (Al) membrane. The theoretical prediction is in quantitative agreement with the atomistic simulations.

In the continuum theory of surface elasticity, a solid surface is treated as a thin layer adhering to the underlying material without slipping.<sup>16,17</sup> The equilibrium and constitutive equations of the bulk are the same as those in the classical elasticity theory, but the boundary conditions must ensure the force balance of the surface layer which results in the surface tension  $\tau_0$ . The elastic constants characterizing

the surface  $E^s$  and  $\nu^s$  are different from those of the bulk material  $E$  and  $\nu$ , where  $E$  and  $\nu$  denote the Young's modulus and Poisson's ratio, respectively. Thus, the free energy of the system is composed of three parts: the bulk energy, the surface tension, and the surface elasticity.<sup>18</sup> While for most materials the contribution of the surface elasticity is small compared to the surface tension,<sup>18</sup> we neglect this part in our present analysis for simplicity.

The load-deflection relation for a plane strain bulge test has been well studied.<sup>19,20</sup> Herein, we extend the analysis by considering the surface effects. A typical setup is shown in the schematic of Fig. 1. The membrane with thickness  $h$  and length  $2a$  is subject to a uniform pressure  $q$ . Particularly,  $h$  is of a few nanometers. Let  $u$ ,  $v$ , and  $w$  denote the displacement component along the  $x$ -,  $y$ -, and  $z$ - directions, respectively. The strains in the mid-plane of the membrane are given by the non-linear plate theory<sup>21</sup>

$$\begin{aligned}\varepsilon_x &= \frac{\partial u}{\partial x} + \frac{1}{2} \left( \frac{\partial w}{\partial x} \right)^2, \\ \varepsilon_y &= \frac{\partial v}{\partial y} + \frac{1}{2} \left( \frac{\partial w}{\partial y} \right)^2, \\ \gamma_{xy} &= \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} + \frac{\partial w}{\partial x} \frac{\partial w}{\partial y}.\end{aligned}\quad (1)$$

Assuming the material is elastic and isotropic, the free energy of the membrane is

$$\begin{aligned}\Pi &= \frac{1}{2} \frac{Eh}{1-\nu^2} \iint \left[ \varepsilon_x^2 + \varepsilon_y^2 + 2\nu\varepsilon_x\varepsilon_y + \frac{1}{2}(1-\nu)\gamma_{xy}^2 \right] dx dy \\ &+ \iint \tau_0(\varepsilon_x + \varepsilon_y) dx dy - \iint q w dx dy.\end{aligned}\quad (2)$$

The first term in Eq. (2) represents the stretching energy of the membrane. The bending energy has been neglected because the deflection is much larger than the thickness of the membrane. The second term represents the contribution from the surface tension, and the third term is the potential

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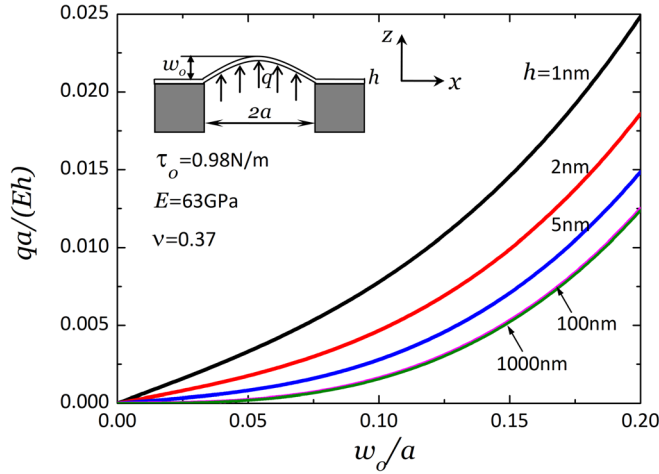


FIG. 1. The theoretical prediction of the load-deflection relation for the nano-scale bulge test on membranes of different thickness. A strong size-dependent behavior presents when the thickness of the membrane is less than 10 nm. As the thickness exceeds about 100 nm, the size effect becomes negligible. Such size dependence is attributed to the effect of the surface tension. The inset sketches the setup of a plain strain bulge test.

energy of the external dead pressure. Herein we focus the analysis on the surface effect and assume a dead load condition that the external pressure is always along the  $z$ -direction. The difference between the dead load and the live load (the pressure is perpendicular to the membrane in the course of deformation) is quantified later.

Minimization of the potential energy in Eq. (2) with respect to the undetermined displacement components leads to a set of governing equations for a membrane. We assume that the membrane size along the  $y$ -direction is much larger; thus, a plane strain condition is set. Therefore the governing equations are reduced to the following forms:

$$\begin{aligned} \frac{dN_t}{dx} &= 0, \\ N_t \frac{d^2w}{dx^2} &= -q, \end{aligned} \quad (3)$$

where  $N_t = N_x + 2\tau_0$ ,  $N_x$  is the in-plane force which relates to the in-plane strain by  $N_x = \frac{Eh}{1-\nu^2} \epsilon_x$ . The first equation in Eq. (3) gives  $N_t = \text{const}$ . Integrating the second equation twice and substituting the clamped boundary conditions  $w(\pm a) = 0$ , it yields  $w(x) = \frac{q}{2N_t}(a^2 - x^2)$ . Inserting  $w(x)$  into Eq. (1) and integrating  $\frac{du}{dx}$  we have  $u(x) = \frac{1-\nu^2}{Eh} N_x x - \frac{q^2 x^3}{6N_t^2} + c$ , where the integral constant  $c$  vanishes because of the boundary condition  $u(0) = 0$ . Setting  $u(\pm a) = 0$ , it gives  $\frac{6}{a^2} \frac{1-\nu^2}{Eh} N_x N_t^2 = q^2$ . Replacing  $N_x$  and  $N_t$  with central deflection  $w_0$  by the relation  $w_0 = \frac{qa^2}{2N_t}$ , we obtain the following load-deflection relation:

$$q = 4\tau_0 \frac{w_0}{a^2} + \frac{4}{3} \frac{w_0^3}{a^4} \frac{Eh}{1-\nu^2}. \quad (4)$$

Once the material parameters  $E$ ,  $\nu$ , and  $\tau_0$  and the geometric parameters  $a$  and  $h$  are given, we can plot the load-deflection curve  $q - w_0$ . Alternatively, for a given set of experimental curves  $q - w_0$  from the bulge test, we can extract the material parameters. Rewrite Eq. (4) in the dimensionless form

$$\frac{qa}{Eh} = \frac{4\tau_0 w_0}{Eh a} + \frac{4}{3} \left(\frac{w_0}{a}\right)^3 \frac{1}{1-\nu^2}. \quad (5)$$

It is clearly seen from the term  $\frac{\tau_0}{Eh}$  of Eq. (5) that the functional dependence of the dimensionless load  $\frac{qa}{Eh}$  on the dimensionless deflection  $\frac{w_0}{a}$  is size dependent. This indicates that it is necessary to vary the thickness of the membrane in the experiments to obtain the bulk and the surface parameters. Alternatively one can obtain the surface parameters from other settings and then calculate the bulk material parameters from the bulge test data. If the surface tension  $\tau_0$  is zero, then Eq. (5) reduces to the classical results for the bulk material.

We perform MD simulations to obtain the material parameters—the Young's modulus, the Poisson's ratio, and the surface tension of an Al membrane via uniaxial tensile simulations. We further model the plane strain bulge test to compare with the theoretical predictions. MD simulations are conducted using the package large-scale atomic/molecular massively parallel simulator (LAMMPS).<sup>22</sup> Al is a face-centered cubic (FCC) crystal with the stiffness constants  $c_{11} = 114.3$  GPa,  $c_{12} = 61.92$  GPa, and  $c_{44} = 31.62$  GPa.<sup>23</sup> The degree of isotropy for a FCC crystal can be characterized by the parameter  $A = 2c_{44}/(c_{11} - c_{12})$ , which measures the ratio of the shear stiffness in the crystal directions of [100] and [110]. When the parameter  $A$  is close to unity, the material is isotropic.<sup>23</sup> For aluminum, the parameter  $A = 1.2$ . Therefore we use Al to model an isotropic material. The modified embedded-atom method (MEAM) potential is adopted to describe the interaction of Al atoms.<sup>24</sup>

We perform uniaxial tensile simulations in the following procedure. We first consider an infinite plate with thickness 2.43 nm subject to a uniaxial stress  $\sigma_x$  in the [100] direction, and periodic boundary conditions are applied in all the three directions. We record the strains and calculate the elastic parameters by  $E = \sigma_x/\epsilon_x$  and  $\nu = -\epsilon_y/\epsilon_x$  and obtain  $E = 63$  GPa and  $\nu = 0.37$ , which are close to the experimental data  $E = 70$  GPa and  $\nu = 0.35$ .<sup>25</sup> We then perform the same simulation with exposed free surfaces along the out-of-plane direction. In this case the surface tension  $\tau_0$  is generated naturally because of the rearrangement of the surface atoms. The surface tension together with the external uniaxial stress produces the deformation

$$\sigma_x - 2\tau_0/h = E\epsilon_x. \quad (6)$$

Again here we have neglected surface elasticity. We obtain the surface tension  $\tau_0 = 0.98$  N/m that is comparable with the first-principles result 0.96 N/m.<sup>18</sup>

Using the material parameters  $E$ ,  $\nu$ , and  $\tau_0$  obtained through the MD simulations, we plot the theoretical load-deflection relation in Fig. 1. A clear size-dependent behavior is seen for the membranes of thickness less than 10 nm. Such size dependence is attributed to the surface tension at nano-scale, and its significance can be exemplified by comparing the load for the membranes of different thickness for a given deflection—the magnitude varies by up to a factor of 4. Furthermore, a strong size effect particularly presents at the initial stage of the load-deflection curve. This can be understood from Eq. (4) that the surface tension term dominates while the cubic term is rather small at this stage. This

behavior is similar to the effect of the residual stress on bulge test,<sup>26,27</sup> but their physical origins are different, and moreover the surface effects induce size dependence while the residual stress effects do not. The term of the residual stress can also be incorporated in Eq. (4), but this will not contribute to our focus on the surface effects. As the thickness exceeds about 100 nm, the surface effects become negligible. The load-deflection curves of membranes of thickness 100 nm and 1000 nm almost coincide. The scale under which surface effects must be considered may be estimated by comparing  $h \sim \tau_0/E$ .

We perform MD simulations on the bulge test to verify the theoretical prediction. We study two membranes under the plane strain condition of the same length of 24.3 nm but of different thickness of 1.2 nm and 1.6 nm, subject to a uniform pressure. The load-deflection relations are plotted in Fig. 2, together with the theoretical prediction using the material parameters from the MD tensile test. The inset shows the image of the MD simulations. The atoms are color-coded by the centrosymmetry parameter.<sup>28</sup> Red spheres represent the surface atoms, and blue spheres represent the bulk atoms. The MD simulations agree remarkably well with the results predicted by the continuum theory of surface elasticity, both of which show clear difference from the classical results which do not consider the surface effects. The MD simulation validates the theoretical prediction, and again as a virtual experiment it shows the importance of the surface effects on nano-scale structures.

If the deflection is larger than the membrane length, the governing equations (3) should be modified to incorporate the effect of live pressure as follows:<sup>19</sup>

$$\begin{aligned} \frac{dN_t}{dx} &= 0, \\ N_t \frac{d^2w}{dx^2} &= -q \left[ 1 + \left( \frac{dw}{dx} \right)^2 \right]^{3/2}. \end{aligned} \quad (7)$$

If the deflection is small, the square of the bending angle  $\frac{dw}{dx}$  is small compared to unity; then, Eq. (7) reduces to Eq. (3).

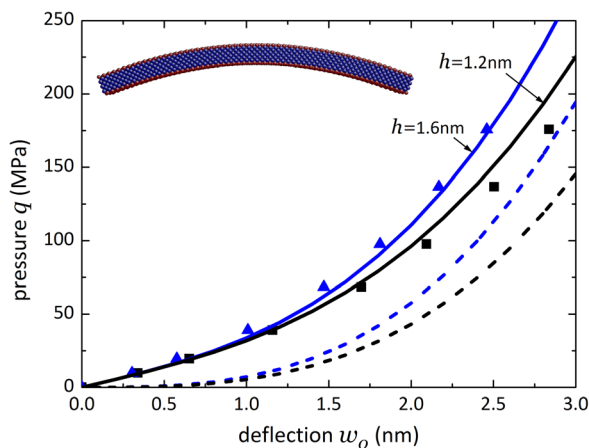


FIG. 2. Load-deflection curves for two samples with different thickness. The solid lines represent the theoretical model considering the surface effect; the dashed lines are the theoretical results without the surface effect; and the markers shows the data in the MD simulations. The inset shows the image of MD simulations. Atoms are color-coded by the centrosymmetry parameter. Red spheres represent the surface atoms, and blue spheres represent the bulk atoms.

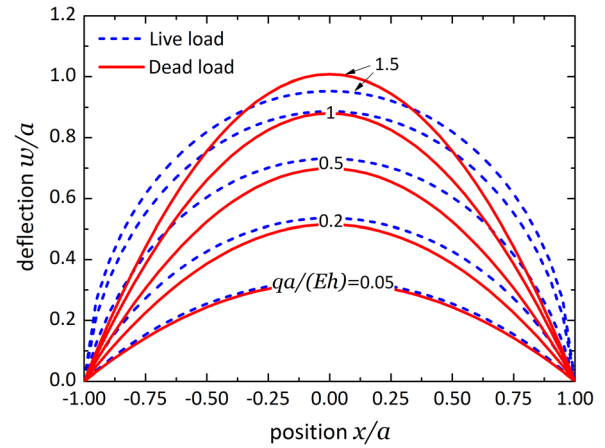


FIG. 3. The deflection profiles under different load conditions according to Eqs. (3) and (7). When the deflection is comparable with the membrane length, the simplified Eq. (3) is a good approximation of Eq. (7) for analysis.

Equation (7) is numerically solved using MATLAB, and the results are shown in Fig. 3. When the dimensionless load  $\frac{qa}{Eh}$  is smaller than 0.05, results of Eqs. (3) and (7) are almost identical. When the load is bigger, the difference shows up. However, as long as the deflection is smaller than the membrane length, the simplified Eq. (3) is a good approximation of Eq. (7) for analysis.

In summary, we investigate the surface effect on nano-scale bulge test based on the continuum theory of surface elasticity and atomistic simulations. We refine the load-deflection relation and illustrate its strong size-dependent nature. Such size effect is prominent for the membranes of thickness less than 10 nm. The theoretical prediction is further validated by the molecular dynamics simulations. We stress that the bulge test for bulk materials is not directly applicable for nano-scale measurements. The modified load-deflection relation enables a nano-scale bulge test to obtain the Young's modulus, the Poisson's ratio, and the surface tension of membranes.

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