Available online at www.sciencedirect.com

International Journal of Solids and Structures 43 (2006) 132–143

www.elsevier.com/locate/ijsolstr

Surface Green function for a soft elastic half-space: Influence of surface stress

L.H. He [a], C.W. Lim [b,*]

[a] *CAS Key Laboratory of Mechanical Behavior and Design of Materials, University of Science and Technology of China, Hefei, Anhui 230027, PR China*
[b] *Department of Building and Construction, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong*

Received 14 August 2004; received in revised form 11 April 2005
Available online 8 June 2005

Abstract

Surface Green function for incompressible, elastically isotropic half-space coupled with surface stress is derived by using double Fourier transform technique. The result indicates that the surface displacement induced by a force tangential to the surface is the same as the usual solution for elastic half-spaces where the effect of surface stress is ignored. However, the displacement caused by a force normal to the surface involves an additional parameter, i.e. the ratio of specific surface stress to shear modulus. The parameter has the dimension of length, and may provide a means to introduce an intrinsic length scale for some related problems regarding the surface of an elastic half-space. This is extremely true for soft elastic media with very low shear modulus, because in that situation the magnitude of the parameter is relatively large. As an illustrative example, the proposed Green function is adopted to analyze the interaction between two molecules with circular section adsorbed on the surface of a soft elastic half-space. It is shown that surface stress remarkably affects the pair interaction potential when the distance between the molecules is not larger than several times of the intrinsic length scale.

Keywords: Green function; Elastic half-space; Surface stress

1. Introduction

Materials like polymer gels are very soft and their mechanical elastic behavior under small deformations can be well characterized by Hooke's law. Since the elastic moduli of such soft solids are much

---

[*] Corresponding author. Tel.: +852 2788 7285; fax: +852 2788 7612.
E-mail address: bccwlim@cityu.edu.hk (C.W. Lim).

0020-7683/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijsolstr.2005.04.026

lower than their metallic counterparts (Radmacher et al., 1995, 1996), discernible deformation patterns can be created on their surface by very small forces. The importance of the topographical patterns was recently highlighted (Assender et al., 2002), the applications can be found in various fields, such as manipulating polymer nanostructures (Peters et al., 2000), directing microfluidic flows (Zhao et al., 2001) and regulating surface self-assembly (Srinivasan et al., 2001). In order to create desired surface profile, deformation of the soft solids should be well understood a prior. Motivated by this reason, the present paper studies the surface deformation of a soft elastic half-space. In particular, surface Green function for the half-space will be derived. Though the Green function for conventional elastic half-space has been well established, the present study further generalizes the model to incorporate the influence of surface stress.

The surface of a solid has different atomistic structure from the bulk and is treated as a specific mathematical surface which has no thickness. The free energy per unit area of the surface is called specific surface energy, and its change per unit amount of strain is referred as surface stress; both have the dimension of force over length. An excellent explanation of the concept of surface stress has been given by Cammarata (1994). To deform a solid, excessive work is needed to stretch the surface in addition to straining the bulk. The larger the partition of work done to surface, the more important the effect of surface stress. Nozieres et al. (2001) suggested that the ratio of specific surface stress to the bulk Young's modulus can be used to roughly reflect the relative importance of surface stress. Obviously, this ratio has the dimension of length, and defines an intrinsic length scale for the material. For usual metallic materials, the ratio is normally less than one Angstrom. The effect of surface stress on the deformation is negligible in many circumstances, especially when the characteristic size of the metals is very large. For soft solids, however, the situation is rather different. The surface stress of a soft solid is a little less than that of a metal, but the elastic modulus can be nearly 7–8 orders smaller than that of conventional solids. Therefore, the corresponding intrinsic length scale of soft solids is much larger, implying that surface stress may play crucial role in affecting the deformation of soft solids. Indeed, a number of unusual phenomena regarding soft solids have been observed experimentally or predicted theoretically. For instance, Pieranski et al. (2000) found that the faceting of their soft crystals composed of non-ionic surfactant molecules is remarkable: up to 60 different facets are present on the equilibrium shape. Nozieres et al. (2001) referred this phenomenon to the influence of surface stress. From theoretical analysis, they also showed that, due to surface stress, a surface step penetrates inside the soft crystal as edge dislocation rather than bound to the surface. In fact, even for usual metallic materials, the effect of surface stress sometimes is significant as well. Recent theoretical studies revel that the presence of surface effect causes the elastic responses of tiny structural elements such as rods (Miller and Shenoy, 2000; Shenoy, 2002) and films (He et al., 2004; Lim and He, 2004) to be significantly size-dependent, when their characteristic size reduces to tens of nanometers.

The present paper is organized as follows. In the next section, the basic equations and boundary conditions for an incompressible, elastically isotropic half-space coupled with surface stress are listed. The surface Green function tensor for the half-space is then derived in Section 3. All components of the Green function are determined explicitly by using the double Fourier transform technique. The result shows that the elastic response of the half-space to a concentrated force tangential to the surface is the same as that predicted by the conventional elasticity theory. Building on this foundation, the surface displacement derived in Section 4 is devoted to illustrate the application of the obtained Green function in calculating the interaction between two adsorbed molecules on the surface. As a primary effort, the possible influence of thermal fluctuation on the energy is not considered. Numerical results indicate that the presence of surface stress leads to remarkable decrease in interaction energy when the distance between the molecules is not greater than a few times of the intrinsic length scale. Thus, it is concluded that there is a need to include the effect of surface stress in analyzing similar problems related to surface deformation of soft solids. The work presented in this paper is briefly summarized in Section 5.

2. Fundamental equations

The physical system being considered is an elastic half-space subject to external forces on the surface. A Cartesian coordinate system (x_1, x_2, x_3) is introduced, so that the x_1–x_2 plane coincides with the undeformed surface and the half-space is represented by $x_3 \leqslant 0$ (Fig. 1). The displacement, stress and strain components are denoted, in sequence, by u_i, σ_{ij} and ε_{ij}. The relations between the strain and displacement components are given by $\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$. Throughout this paper, the usual summation convention is adopted for repeated indices, where Latin indices run from 1 to 3 while Greek ones take the value of 1 or 2. A comma denotes differentiation with respect to the suffix coordinates.

The main concern of the present paper is to incorporate the influence of surface stress. Despite the extensive discussion surface stress has received over the years, there remains a great deal of confusion concerning its meaning and importance (Cammarata, 1994). A rigorous derivation of the model for elastically isotropic solids with surface stress is due to Gurtin and Murdoch (1975). The model is very general in the sense that it allows for different elastic property of the surface from the bulk. This paper will not involve such a general case and assumes that the surface of the half-space has the same elastic property as its interior. Then the surface stress components of the flat surface read (Gurtin and Murdoch, 1975, 1978)

$$\begin{aligned} \tau_{\alpha\beta} &= \tau[(1 + u_{v,v})\delta_{\alpha\beta} - u_{\beta,\alpha}], \\ \tau_{3\beta} &= \tau u_{3,\beta}, \end{aligned} \tag{1}$$

in which $\delta_{\alpha\beta}$ is the usual Kronecker delta, and τ is the residual surface stress (i.e., the surface stress in the case that the surface is not deformed).

It is presumed that the soft half-space is elastic and incompressible, i.e. $u_{k,k} = 0$. The stress within it obeys the equilibrium equation

$$\sigma_{ij,j} = 0, \tag{2}$$

and assuming elastic incompressibility, the constitutive law is written as

$$\sigma_{ij} = -p\delta_{ij} + 2\mu\varepsilon_{ij}, \tag{3}$$

where $p = -\sigma_{kk}/3$ is the hydrostatic pressure, μ is shear modulus. On the surface of the half-space, $x_3 = 0$, force balance requires $\sigma_{i3} = \tau_{i\alpha,\alpha} + q_i$. This last condition can also be expressed, by the substitution of Eq. (1), as follows

$$\sigma_{\alpha 3} = q_\alpha, \quad \sigma_{33} = \tau u_{3,\alpha\alpha} + q_3. \tag{4}$$

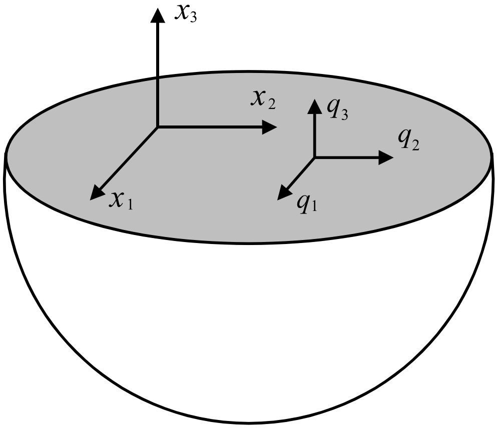

Fig. 1. A soft elastic half-space subject to external force on the surface.

Eqs. (2)–(4) along with the incompressibility condition $u_{k,k} = 0$ completely describe the deformation of the half-space. It is clear that the presence of the surface stress gives rise to the non-classical boundary conditions in Eq. (4) which are coupled with the displacement field within the bulk material. The same form of boundary conditions have also been used by several authors in the study on some problems relevant to surface effects (e.g. Shenoy and Sharma, 2002; Koguchi, 2003; Kumar, 2003; Yang, 2004).

3. Derivation of Green function

Surface Green function $G_{ij}(x_1 - x_1', x_2 - x_2', 0)$ of the half-space is defined as the x_i-component of displacement at $(x_1, x_2, 0)$ on the surface that is induced by a unit force applied at $(x_1', x_2', 0)$ along x_j direction. The objective of this section is to derive the Green function by using double Fourier transform technique. For convenience, the special case that the unit force is applied at the origin (i.e. $x_1' = 0$ and $x_2' = 0$) will be considered. Through the obtained solution $G_{ij}(x_1, x_2, 0)$, the Green function for the general case that $(x_1', x_2', 0)$ does not coincide with the origin can be generated simply by replacing x_1 and x_2, respectively, by $x_1 - x_1'$ and $x_2 - x_2'$. To this end, three sets of unit external forces on the surface of the half-space are taken into account:

$$q_1 = \delta(x_1)\delta(x_2), \quad q_2 = q_3 = 0; \tag{5}$$

$$q_2 = \delta(x_1)\delta(x_2), \quad q_1 = q_3 = 0; \tag{6}$$

$$q_3 = \delta(x_1)\delta(x_2), \quad q_1 = q_2 = 0; \tag{7}$$

where $\delta(x)$ stands for Dirac's source function. The solutions to the boundary value problems corresponding to the conditions (5)–(7) determine $G_{i1}(x_1, x_2, 0)$, $G_{i2}(x_1, x_2, 0)$ and $G_{i3}(x_1, x_2, 0)$, respectively.

By substituting Eq. (3) into Eq. (2) and making use of the strain–displacement relations and the incompressibility condition, it is obtained that

$$\mu\nabla^2 u_i - p_{,i} = 0, \quad u_{k,k} = 0. \tag{8}$$

The solution to these equations can be represented by the double Fourier integrals of the form

$$\begin{aligned} u_i &= \frac{1}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{U}_i(\xi_1, \xi_2, x_3)\mathrm{e}^{-\mathrm{i}\xi_\alpha x_\alpha}\mathrm{d}\xi_1\mathrm{d}\xi_2, \\ p &= \frac{1}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{P}(\xi_1, \xi_2, x_3)\mathrm{e}^{-\mathrm{i}\xi_\alpha x_\alpha}\mathrm{d}\xi_1\mathrm{d}\xi_2, \end{aligned} \tag{9}$$

where $\mathrm{i} = \sqrt{-1}$, and $\overline{U}_i$ and $\overline{P}$ are double Fourier transforms of u_i and p, respectively, defined by

$$\begin{aligned} \overline{U}_i &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} u_i(x_1, x_2, x_3)\mathrm{e}^{\mathrm{i}\xi_\alpha x_\alpha}\mathrm{d}x_1\mathrm{d}x_2, \\ \overline{P} &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p(x_1, x_2, x_3)\mathrm{e}^{\mathrm{i}\xi_\alpha x_\alpha}\mathrm{d}x_1\mathrm{d}x_2. \end{aligned} \tag{10}$$

Inserting Eq. (9) into Eq. (8) gives

$$\begin{aligned} &\mu(\overline{U}_{\alpha,33} - \xi^2\overline{U}_\alpha) + \mathrm{i}\xi_\alpha\overline{P} = 0, \\ &\mu(\overline{U}_{3,33} - \xi^2\overline{U}_3) - \overline{P}_{,3} = 0, \\ &\overline{U}_{3,3} - \mathrm{i}\xi_\alpha\overline{U}_\alpha = 0, \end{aligned} \tag{11}$$

with $\xi^2 = \xi_1^2 + \xi_2^2$. The general solution of the above ordinary differential equations can be obtained readily, and the result is

$$
\begin{aligned}
\overline{U}_1 &= \left[\mathrm{i}\xi_1\left(x_3 - \frac{1}{2\xi}\right)C_1 + \left(1 - \frac{1-2\xi x_3}{2\xi^2}\xi_1^2\right)C_2 - \frac{1-2\xi x_3}{2\xi^2}\xi_1\xi_2 C_3\right]\mathrm{e}^{\xi x_3},\\
\overline{U}_2 &= \left[\mathrm{i}\xi_2\left(x_3 - \frac{1}{2\xi}\right)C_1 - \frac{1-2\xi x_3}{2\xi^2}\xi_1\xi_2 C_2 + \left(1 - \frac{1-2\xi x_3}{2\xi^2}\xi_2^2\right)C_3\right]\mathrm{e}^{\xi x_3},\\
\overline{U}_3 &= \left[\left(\frac{3}{2} - \xi x_3\right)C_1 + \mathrm{i}\xi_1\left(x_3 - \frac{1}{2\xi}\right)C_2 + \mathrm{i}\xi_2\left(x_3 - \frac{1}{2\xi}\right)C_3\right]\mathrm{e}^{\xi x_3},\\
\overline{P} &= -2\mu(\xi C_1 - \mathrm{i}\xi_1 C_2 - \mathrm{i}\xi_2 C_3),
\end{aligned}
\tag{12}
$$

where C_1, C_2 and C_3 are yet unknown functions of ξ_1 and ξ_2. For each set of external forces given in Eqs. (5)–(7), the functions can be determined by using the boundary conditions on the surface. To do so, one can substitute one of Eqs. (5)–(7) into (4), invoke Eqs. (3), (9) and (12), and then take the inverse double Fourier transform with respect to the resulting equations. This leads to a linear system composed of three algebraic equations related to C_1, C_2 and C_3. Solving it immediately provides the expression of the displacement field of the half-space. The results are given in the following.

For the external force on the surface given in Eq. (5), the unknowns C_1, C_2 and C_3 are be obtained as

$$
C_1 = \frac{\mathrm{i}\xi_1}{4\mu\xi^2}, \quad C_2 = \frac{3\xi^2 + \xi_2^2}{4\mu\xi^3}, \quad C_3 = -\frac{\xi_1\xi_2}{4\mu\xi^3}. \tag{13}
$$

Inserting the result into (12) and then into (9) yields

$$
\begin{aligned}
u_1 &= \frac{1}{8\pi^2\mu}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\xi^2 + \xi_2^2 + \xi\xi_1^2 x_3}{\xi^3}\mathrm{e}^{\xi x_3 - \mathrm{i}\xi_\alpha x_\alpha}\mathrm{d}\xi_1\mathrm{d}\xi_2,\\
u_2 &= -\frac{1}{8\pi^2\mu}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{(1-\xi x_3)\xi_1\xi_2}{\xi^3}\mathrm{e}^{\xi x_3 - \mathrm{i}\xi_\alpha x_\alpha}\mathrm{d}\xi_1\mathrm{d}\xi_2,\\
u_3 &= \frac{\mathrm{i}}{8\pi^2\mu}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\xi_1 x_3}{\xi}\mathrm{e}^{\xi x_3 - \mathrm{i}\xi_\alpha x_\alpha}\mathrm{d}\xi_1\mathrm{d}\xi_2.
\end{aligned}
\tag{14}
$$

These displacement components do not involve any contribution from the surface stress τ. On the surface $x_3 = 0$, the above integrals can be estimated explicitly, and the displacement components are derived as

$$
u_1 = \frac{1}{4\pi\mu}\left(\frac{1}{r} + \frac{x_1^2}{r^3}\right), \quad u_2 = \frac{1}{4\pi\mu}\frac{x_1x_2}{r^3}, \quad u_3 = 0 \tag{15}
$$

in which $r = \sqrt{x_1^2 + x_2^2}$. Hence one gets the following components of surface Green function tensor:

$$
G_{11}(x_1,x_2,0) = \frac{1}{4\pi\mu}\left(\frac{1}{r} + \frac{x_1^2}{r^3}\right), \quad G_{21}(x_1,x_2,0) = \frac{1}{4\pi\mu}\frac{x_1x_2}{r^3}, \quad G_{31}(x_1,x_2,0) = 0. \tag{16}
$$

For the set of external forces given in Eq. (6), the solution of the unknowns is as follows

$$
C_1 = \frac{\mathrm{i}\xi_2}{4\mu\xi^2}, \quad C_2 = -\frac{\xi_1\xi_2}{4\mu\xi^3}, \quad C_3 = \frac{3\xi^2 + \xi_1^2}{4\mu\xi^3}, \tag{17}
$$

and the corresponding displacement field is expressed by

$$\begin{aligned}
u_1 &= -\frac{1}{8\pi^2\mu}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{(1-\xi x_3)\xi_1\xi_2}{\xi^3}\mathrm{e}^{\xi x_3-\mathrm{i}\xi_\alpha x_\alpha}\mathrm{d}\xi_1\mathrm{d}\xi_2,\\
u_2 &= \frac{1}{8\pi^2\mu}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\xi^2+\xi_1^2+\xi\xi_2^2x_3}{\xi^3}\mathrm{e}^{\xi x_3-\mathrm{i}\xi_\alpha x_\alpha}\mathrm{d}\xi_1\mathrm{d}\xi_2,\\
u_3 &= \frac{\mathrm{i}}{8\pi^2\mu}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\xi_2 x_3}{\xi}\mathrm{e}^{\xi x_3-\mathrm{i}\xi_\alpha x_\alpha}\mathrm{d}\xi_1\mathrm{d}\xi_2.
\end{aligned} \tag{18}$$

In particular, the displacement components of a point on the surface of the half-space can be written in the explicit form as

$$u_1 = \frac{1}{4\pi\mu}\frac{x_1x_2}{r^3}, \quad u_2 = \frac{1}{4\pi\mu}\left(\frac{1}{r}+\frac{x_2^2}{r^3}\right), \quad u_3 = 0, \tag{19}$$

which further provide that

$$G_{12}(x_1,x_2,0) = \frac{1}{4\pi\mu}\frac{x_1x_2}{r^3}, \quad G_{22}(x_1,x_2,0) = \frac{1}{4\pi\mu}\left(\frac{1}{r}+\frac{x_2^2}{r^3}\right), \quad G_{32}(x_1,x_2,0) = 0. \tag{20}$$

As expected, the results are independent of the surface stress.

For the external force specified by Eq. (7), it can be arrived at

$$C_1 = \frac{1}{2\mu(2+\eta\xi)\xi}, \quad C_2 = \frac{\mathrm{i}\xi_1}{2\mu(2+\eta\xi)\xi}, \quad C_3 = \frac{\mathrm{i}\xi_2}{2\mu(2+\eta\xi)\xi} \tag{21}$$

in which $\eta = \tau/\mu$ is a constant having the dimension of length. Accordingly, the displacement field of the half-space is

$$\begin{aligned}
u_1 &= \frac{\mathrm{i}}{8\pi^2\mu}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\xi_1 x_3}{(2+\eta\xi)\xi}\mathrm{e}^{\xi x_3-\mathrm{i}\xi_\alpha x_\alpha}\mathrm{d}\xi_1\mathrm{d}\xi_2,\\
u_2 &= \frac{\mathrm{i}}{8\pi^2\mu}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\xi_2 x_3}{(2+\eta\xi)\xi}\mathrm{e}^{\xi x_3-\mathrm{i}\xi_\alpha x_\alpha}\mathrm{d}\xi_1\mathrm{d}\xi_2,\\
u_3 &= \frac{1}{8\pi^2\mu}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{1-\xi x_3}{(2+\eta\xi)\xi}\mathrm{e}^{\xi x_3-\mathrm{i}\xi_\alpha x_\alpha}\mathrm{d}\xi_1\mathrm{d}\xi_2.
\end{aligned} \tag{22}$$

It can be seen that on the surface $x_3 = 0$ the above expressions become

$$u_1 = 0, \quad u_2 = 0, \quad u_3 = \frac{1}{4\pi^2\mu}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\mathrm{e}^{-\mathrm{i}\xi_\alpha x_\alpha}}{(2+\eta\xi)}\mathrm{d}\xi_1\mathrm{d}\xi_2. \tag{23}$$

The integral in the last equation can be estimated by letting $x_1 = r\cos\theta$, $x_2 = r\sin\theta$, $\xi_1 = \xi\cos\psi$, $\xi_2 = r\sin\psi$ and recalling the integral representation of Bessel function of the first kind with order zero (Jerri, 1992):

$$J_0(\xi r) = \frac{1}{2\pi}\int_0^{2\pi}\mathrm{e}^{-\mathrm{i}\xi r\cos(\theta-\psi)}\mathrm{d}\theta. \tag{24}$$

In this situation u_3 can be represented in term of a J_0-Hankel transform $\int_0^\infty J_0(\xi r)/(2+\eta\xi)\mathrm{d}\xi$ and is finally obtained as (Erdelyi et al., 1954)

$$u_3 = \frac{1}{4\pi\mu\eta}\left[\frac{4r}{\eta}{}_1F_2\left(1;\frac{3}{2},\frac{3}{2};-\frac{r^2}{\eta^2}\right) - \pi Y_0\left(\frac{2r}{\eta}\right)\right], \tag{25}$$

where ${}_pF_q(a_1, \ldots a_p; b_1, \ldots b_q; x)$ is the generalized hypergeometric function (see Andrews, 1985), and $Y_0(x)$ is the Bessel function of the second kind with order zero. Accordingly, one has the results

$$\begin{aligned} &G_{13}(x_1, x_2, 0) = 0, \quad G_{23}(x_1, x_2, 0) = 0, \\ &G_{33}(x_1, x_2, 0) = \frac{1}{4\pi\mu\eta}\left[\frac{4r}{\eta}\,{}_1F_2\left(1; \frac{3}{2}, \frac{3}{2}; -\frac{r^2}{\eta^2}\right) - \pi Y_0\left(\frac{2r}{\eta}\right)\right]. \end{aligned} \tag{26}$$

Eqs. (16), (20) and (26) provide all the components of the surface Green function tensor for the half-space. Clearly, the Green function tensor is symmetric in the sense $G_{ij}(x_1, x_2, 0) = G_{ji}(x_1, x_2, 0)$. Only $G_{33}(x_1, x_2, 0)$ involves the parameter η having the dimension of length, meaning that the normal displacement due to a concentrated force normal to the surface is influenced by surface stress. The other components of the surface Green function tensor are the same as those for a usual incompressible, elastically isotropic half-space where the effect of surface stress is ignored. In the limiting case of $\eta = 0$, from Eq. (23) it is seen that $G_{33}(x_1, x_2, 0)$ also becomes the well-known result for a half-space without surface effect, i.e. $G_{33}(x_1, x_2, 0) = 1/4\pi\mu r$ (Ling et al., 2002).

4. Application: interaction of two adsorbed molecules

For the application of the derived surface Green function, interaction between two adsorbed large molecules mediated by the underlying soft elastic half-space is analyzed as an illustrative example. Since the main objective of this paper is to show the effect of surface stress, the possible influence of thermal fluctuations will not be included for simplicity. As pointed out by Schiller and Mogel (2001), a molecule adsorbed on the surface of a soft elastic body may sink into the half-space (Fig. 2a) or mould around the interface (Fig. 2b), depending on the nature of adsorption. The molecule exerts a distribution of normal force on the surface. In the latter case, the resultant force on the molecule vanishes, while in the former case the molecule sustains a net force towards the elastic body. Schiller and Mogel (2001) have studied the interaction between colloidal molecules adsorbed on soft elastic film resting on a rigid substrate, but the effect of surface stress was not incorporated.

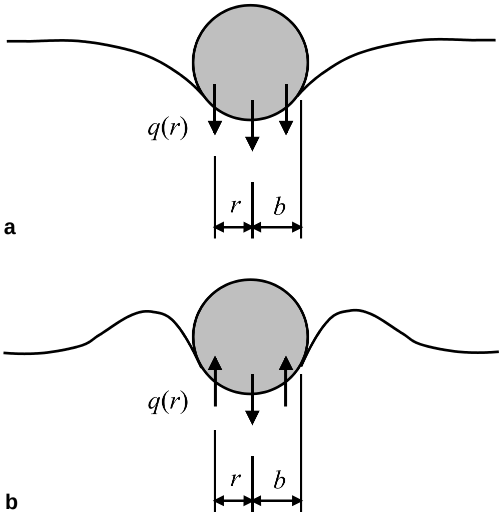

Fig. 2. Adsorption of a molecule on the surface of a soft solid: (a) the molecule is unbalanced and sinks into the solid; (b) the molecule is balanced and surface of the solid moulds around it.

In order to account for the influence of surface stress, the net variation in energy caused by adsorption of molecules is considered. Assume that the adsorbed molecules exert distributed normal force q_3 on the surface region S_0 where they are in contact with the half-space. Then, following Gurtin and Murdoch (1975), the total free energy of the system reads

$$U = \int_V \frac{1}{2}\sigma_{ij}u_{i,j}\mathrm{d}V + \int_S \frac{1}{2}(\tau_{i\alpha} - \tau\delta_{i\alpha})u_{i,\alpha}\mathrm{d}S + \int_S \tau u_{\alpha,\alpha}\mathrm{d}S - \int_{S_0} q_3u_3\mathrm{d}S \tag{27}$$

in which the first integral is the strain energy, the second and third integrals stand for the work done by the residual surface stress, and the last one is the potential energy of the external force. Upon the use of Gauss theorem and Eqs. (1) and (4), it can be proved that the variation in energy resulted from adsorption can be written as

$$U = -\frac{1}{2}\int_{S_0} q_3u_3\mathrm{d}S. \tag{28}$$

If there are two molecules adsorbed on the surface, they exert two distributed forces $q_3^{(1)}$ and $q_3^{(2)}$ on the surface regions S_1 and S_2, respectively. The total displacement field of the half-space is the superposition of the displacement induced by the first molecule alone, $u_i^{(1)}$, and that by the second molecule alone, $u_i^{(2)}$. It is easy to know that the interaction energy between the two molecules, i.e. the total energy variation caused by the two adsorbed molecules minus the respective energy variation caused by each molecule alone, can be expressed in the form

$$U_{12} = -\frac{1}{2}\int_{S_1} q_3^{(1)}u_3^{(2)}\mathrm{d}S - \frac{1}{2}\int_{S_2} q_3^{(2)}u_3^{(1)}\mathrm{d}S. \tag{29}$$

Since $u_3^{(j)}(\boldsymbol{y}_j) = \int_{S_j} g(\boldsymbol{y}_1 - \boldsymbol{y}_2)q_3^{(j)}(\boldsymbol{y}_j)\mathrm{d}S_j$ $(j = 1,2)$, one can see that the two terms in the above equation are equal, and the interaction energy can be written alternatively as

$$U_{12} = -\int_{S_1}\int_{S_2} q_3^{(1)}(\boldsymbol{y}_1)g(\boldsymbol{y}_1 - \boldsymbol{y}_2)q_3^{(2)}(\boldsymbol{y}_2)\mathrm{d}S_1\mathrm{d}S_2. \tag{30}$$

Here $g(\boldsymbol{y}_1-\boldsymbol{y}_2) = G_{33}(\boldsymbol{y}_1-\boldsymbol{y}_2)$, $\boldsymbol{y}_1$ and $\boldsymbol{y}_2$ are arbitrary points belonging to S_1 and S_2, respectively.

For simplicity, it is assumed that the molecules have a circular cross section in the direction perpendicular to the surface. The contact regions S_1 and S_2 then are circular, with the centers $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ as well as radii b_1 and b_2, respectively, as shown in Fig. 3. In this situation the distributed force exerted by each molecule is axisymmetric about the center of contact region, and the interaction energy can be represented as follows

$$U_{12} = -\int_0^{b_1}\int_0^{b_2}\int_0^{2\pi}\int_0^{2\pi} q_3^{(1)}(\rho_1)q_3^{(2)}(\rho_2)g(\boldsymbol{r}+\boldsymbol{l})\rho_1\rho_2\mathrm{d}\theta_1\mathrm{d}\theta_2\mathrm{d}\rho_1\mathrm{d}\rho_2, \tag{31}$$

where $\boldsymbol{r} = \boldsymbol{x}_2-\boldsymbol{x}_1$, $\boldsymbol{\rho}_1 = \boldsymbol{y}_1-\boldsymbol{x}_1$, $\boldsymbol{\rho}_2 = \boldsymbol{y}_2-\boldsymbol{x}_2$, $\boldsymbol{l} = \boldsymbol{\rho}_2-\boldsymbol{\rho}_1$, $\rho_1 = |\boldsymbol{\rho}_1|$, $\rho_2 = |\boldsymbol{\rho}_2|$, θ_1 is the angle between $\boldsymbol{\rho}_1$ and $\boldsymbol{r}$, and θ_2 the angle between $\boldsymbol{\rho}_2$ and $\boldsymbol{r}$. For the case when the distance between the centers of the two molecules

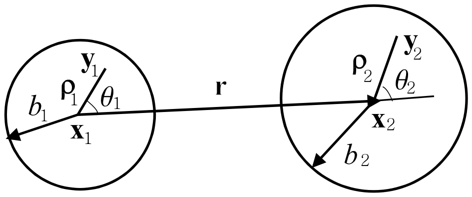

Fig. 3. Sketch for the contact regions of two circularly symmetric molecules adsorbed on the surface.

is significantly large than the radii of the contact regions, it is reasonable to expand the Green function in Taylor's series

$$g(\boldsymbol{r}+\boldsymbol{l}) = g(\boldsymbol{r}) + g_{,\alpha}(\boldsymbol{r})l_\alpha + \frac{1}{2!}g_{,\alpha\beta}(\boldsymbol{r})l_\alpha l_\beta + \frac{1}{3!}g_{,\alpha\beta\nu}(\boldsymbol{r})l_\alpha l_\beta l_\nu + \cdots. \tag{32}$$

With the help of the equalities

$$\begin{aligned}
&\int_0^{2\pi}\int_0^{2\pi} g_{,\alpha}(\boldsymbol{r})l_\alpha \mathrm{d}\theta_1\mathrm{d}\theta_2 = 0,\\
&\int_0^{2\pi}\int_0^{2\pi} g_{,\alpha\beta}(\boldsymbol{r})l_\alpha l_\beta \mathrm{d}\theta_1\mathrm{d}\theta_2 = 2\pi^2(\rho_1^2+\rho_2^2)\nabla_s^2 g(\boldsymbol{r}),\\
&\int_0^{2\pi}\int_0^{2\pi} g_{,\alpha\beta\nu}(\boldsymbol{r})l_\alpha l_\beta l_\nu \mathrm{d}\theta_1\mathrm{d}\theta_2 = 0,\\
&\int_0^{2\pi}\int_0^{2\pi} g_{,\alpha\beta\nu\lambda}(\boldsymbol{r})l_\alpha l_\beta l_\nu l_\lambda \mathrm{d}\theta_1\mathrm{d}\theta_2 = \frac{3}{2}\pi^2(\rho_1^4+\rho_2^4+4\rho_1^2\rho_1^2)\nabla_s^2\nabla_s^2 g(\boldsymbol{r}),
\end{aligned} \tag{33}$$

where $r = |\boldsymbol{r}|$ and $\nabla_s^2 = \mathrm{d}^2/\mathrm{d}r^2 + \mathrm{d}/r\mathrm{d}r$, one gets

$$\int_0^{2\pi}\int_0^{2\pi} g(\boldsymbol{r}+\boldsymbol{l})\mathrm{d}\theta_1\mathrm{d}\theta_2 = (2\pi)^2\left[g(\boldsymbol{r}) + \frac{1}{4}(\rho_1^2+\rho_2^2)\nabla_s^2 g(\boldsymbol{r}) + \frac{1}{64}(\rho_1^4+\rho_2^4+4\rho_1^2\rho_1^2)\nabla_s^2\nabla_s^2 g(\boldsymbol{r}) + \cdots\right]. \tag{34}$$

Hence, the interaction energy is obtained as

$$\begin{aligned}
U_{12} = {}& -P_0^{(1)}P_0^{(2)}g(\boldsymbol{r}) - \frac{1}{4}(P_2^{(1)}P_0^{(2)} + P_0^{(1)}P_2^{(2)})\nabla_s^2 g(\boldsymbol{r}) - \frac{1}{64}(P_4^{(1)}P_0^{(2)} + P_0^{(1)}P_4^{(2)} + 4P_2^{(1)}P_2^{(2)})\nabla_s^2\nabla_s^2 g(\boldsymbol{r})\\
&- \cdots
\end{aligned} \tag{35}$$

in which $P_n^{(j)}$ $(j = 1, 2)$ are the n-th order moments of the normal force defined by

$$P_n^{(j)} = 2\pi\int_0^{b_j} \rho_j^{n+1} q_3^{(j)}(\rho_j)\mathrm{d}\rho_j. \tag{36}$$

These moments may be obtained by properly designed experiments or atomistic calculations. In particular, $P_0^{(j)}$ are also named as adsorption forces which equal zero when the molecules are balanced (Fig. 2a) and do not vanish when the molecules are unbalanced (Fig. 2b). If the two molecules are the same, then $q_3^{(1)} = q_3^{(2)}$, $b_1 = b_2$ and $P_n^{(1)} = P_n^{(2)} = P_n$, and the interaction energy becomes

$$U_{12} = -P_0^2 g(\boldsymbol{r}) - \frac{1}{2}P_0P_2\nabla_s^2 g(\boldsymbol{r}) - \frac{1}{32}(P_0P_4 + 4P_2^2)\nabla_s^2\nabla_s^2 g(\boldsymbol{r}) - \cdots. \tag{37}$$

In order to examine the influence of surface stress on the interaction energy, consider now two identical molecules bound to a soft surface. The surface stress and shear modulus of the half-space are taken as $\tau \sim 0.1$ N/m and $\mu = 1$ MPa, respectively. Then the parameter of length dimension, η, is of the order of 0.1 μm. When the molecules are unbalanced ($P_0 \neq 0$), the first term in Eq. (37) dominates, i.e. $U_{12} = -P_0^2 g(\boldsymbol{r})$, because the higher-order derivatives of the Green function decay rapidly with increasing spacing between the molecules and thus can be neglected. When the molecules are balanced ($P_0 = 0$), the dominating part of the interaction energy becomes $U_{12} = -\frac{1}{8}P_2^2\nabla_s^2\nabla_s^2 g(\boldsymbol{r})$ due to the same reason. In both cases the corresponding interaction energy in absence of surface energy, U_{12}^0, can be calculated by the substitution of $g(\boldsymbol{r}) = 1/4\pi\mu r$. Depicted in Figs. 4 and 5 are variations in the relative interaction energy, U_{12}/U_{12}^0, with the dimensionless distance between the molecules, r/η, for unbalanced ($P_0 \neq 0$) and balanced ($P_0 = 0$) adsorptions, respectively. Since U_{12}/U_{12}^0 only depend on the ratio of r/η, the shape of the curves

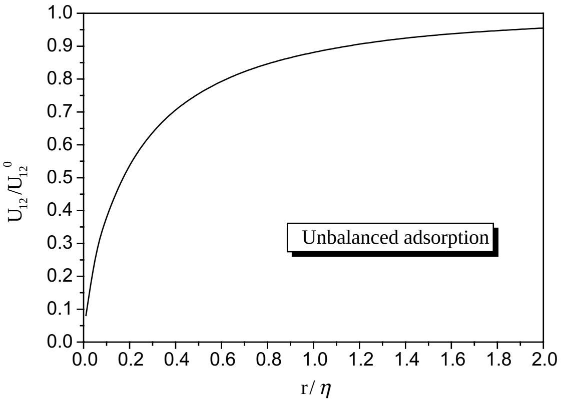

Fig. 4. Variation in the relative interaction energy between two unbalanced adsorbed molecules ($P_0 \neq 0$) with distance.

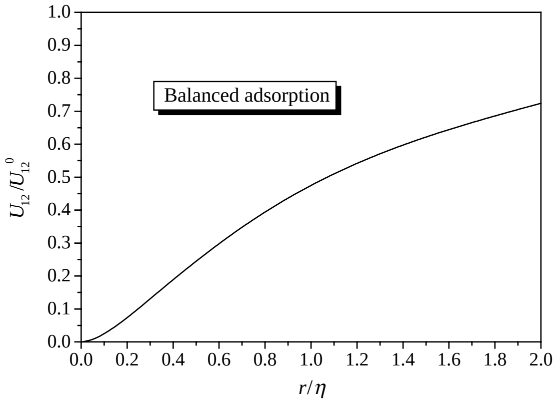

Fig. 5. Variation in the relative interaction energy between two balanced adsorbed molecules ($P_0 = 0$) with distance.

are independent of any material constants of the elastic half-space. For either $P_0 \neq 0$ or $P_0 = 0$, the relative interaction energy approaches unity with the increase of molecule spacing, implying that surface energy has negligible influence on the interaction energy when the two molecules are largely apart. However, when the distance between the adsorbed molecules are small, say two times of η, the presence of surface energy results in remarkable reduction of the interaction energy. The phenomenon can be explained as follows. In fact, the molecules interact with each other through the underlying soft solid, and the indirect interaction force depends on the deformation-induced surface profile around the adsorbed molecules. In the example considered here, the surface stress tends to flatten the surface so as to reduce the surface area and thus the energy. Therefore, the surface becomes more rigid and weakens the indirect interaction between the adsorbed molecules.

5. Conclusions

Incorporating the effect of surface stress, surface Green function for an incompressible, elastically isotropic half-space has been derived by using the double Fourier transform technique. It is seen that the displacement components of the surface caused by a tangential unit force are the same as the usual ones which are obtained in absence of surface stress. In contrast, the displacement component caused by a normal unit force is very different. It is expressed in term of the generalized hypergeometric function, and involves a parameter having the dimension of length defined by the ratio of the surface stress to shear modulus of the half-space. When the elastic half-space is relatively soft, the magnitude of the parameter is quite large. Consequently, the parameter provides an intrinsic length scale in describing surface deformations of soft solids. As an illustrative example, the pair interaction potential between two colloidal molecules adsorbed on the surface of a soft solid is calculated. The result indicates that surface stress strongly influence the mutual interaction between the molecules when their spacing is not larger than several times of the intrinsic length.

Acknowledgements

The work described in this paper was supported by the National Natural Science Foundation of China (Grant No. 10472109) and YJS funding of City University of Hong Kong. We are grateful to a referee for the helpful comment and for pointing out some mistypes in our original manuscript.

References

Andrews, L.C., 1985. Special Functions of Mathematics for Engineers. McGraw-Hill, New York.

Assender, H., Bliznyuk, V., Porfyrakis, K., 2002. How surface topography relates to materials properties. Science 297 (5583), 973–976.

Cammarata, R.C., 1994. Surface and interface stress effects in thin films. Progress in Surface Science 46 (1), 1–38.

Erdelyi, A., Oberhettinger, M.F., Tricomi, F.G., 1954. Tables of Integral Transforms. McGraw-Hill, New York.

Gurtin, M.E., Murdoch, A., 1975. A continuum theory of elastic material surfaces. Archive for Rational Mechanics and Analysis 57 (3), 291–323.

Gurtin, M.E., Murdoch, A., 1978. Surface stress in solids. International Journal of Solids and Structures 14 (5), 43140.

He, L.H., Lim, C.W., Wu, B.S., 2004. A continuum model for size-dependent deformation of elastic films of nano-scale thickness. International Journal of Solids and Structures 41 (3–4), 847–857.

Jerri, A.J., 1992. Integral and Discrete Transforms with Applications and Error Analysis. Marcel Dekker, New York.

Koguchi, H., 2003. Surface deformation induced by a variation in surface stresses in anisotropic half-regions. Philosophical Magazine 83 (10), 1205–1226.

Kumar, S., 2003. Deformation of soft elastomeric layers by periodic interfacial tension gradients. Langmuir 19 (6), 2473–2478.

Lim, C.W., He, L.H., 2004. Size-dependent nonlinear response of thin elastic films with nano-scale thickness. International Journal of Mechanical Sciences 46 (11), 1715–1726.

Ling, F.F., Lai, W.M., Lucca, D.A., 2002. Foundations of Surface Mechanics. Springer, Heidelberg.

Miller, R.E., Shenoy, V.B., 2000. Size-dependent elastic properties of nanosized structural elements. Nanotechnology 11 (3), 139–147.

Nozieres, P., Pistolesi, F., Balibar, S., 2001. Step and facets at the surface of soft crystals. The European Physical Journal B 24 (3), 387–394.

Peters, R.D., Yang, X.M., Wang, Q., de Pablo, J.J., Nealey, P.F., 2000. Combining advanced lithographic techniques and self-assembly of thin films of diblock copolymers to produce templates for nanofabrication. Journal of Vacuum Sciences & Technology B 18 (6), 3530–3534.

Pieranski, P., Sotta, P., Rohe, D., Imperor-Clerc, M., 2000. Devil's staircase-type of a cubic lyotropic liquid crystal. Physical Review Letters 84 (11), 2409–2412.

Radmacher, M., Fritz, M., Hansma, P.K., 1995. Imaging soft samples with the atomic-force microscope: gelatin in water and propanol. Biophysical Journal 69 (1), 264–270.

Radmacher, M., Fritz, M., Kacher, C.M., Cleveland, J.P., Hansma, P.K., 1996. Measuring the viscoelastic properties of human platelets with the atomic force microscope. Biophysical Journal 70 (1), 556–567.

Shenoy, V.B., 2002. Size-dependent rigidities of nanosized torsional elements. International Journal of Solids and Structures 39 (15), 4039–4052.

Shenoy, V., Sharma, A., 2002. Stability of a thin elastic film interacting with a contactor. Journal of Mechanics and Physics of Solids 50 (5), 1155–1173.

Schiller, P., Mogel, H.J., 2001. Interaction of colloidal molecules adsorbed on soft solid films. Molecular Physics 99 (9), 727–734.

Srinivasan, U., Liepmann, D., Howe, R.T., 2001. Microstructure to substrate self-assembly using capillary forces. Journal of Microelectromechanical Systems 10 (1), 17–24.

Yang, F.Q., 2004. Size-dependent effective modulus of elastic composite materials: spherical nanocavities at dilute concentrations. Journal of Applied Physics 95 (7), 3516–3520.

Zhao, B., Moore, J.S., Beebe, D.J., 2001. Surface-directed liquid flow inside microchannels. Science 291 (5506), 1023–1026.