Colloids and Surfaces A: Physicochem. Eng. Aspects 448 (2014) 175–180

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Line tension at curved edge of a molecular solid

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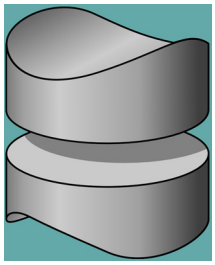
HIGHLIGHTS

- Local cohesive force is calculated in a nano-slit between coaxial cylinders with dispersion forces.
- Distribution of local thermodynamic surface tension on the slit wall is obtained.
- Line tension at the slit rim is estimated as a function of the cylinder radius.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 January 2014
Received in revised form 2 February 2014
Accepted 7 February 2014
Available online 17 February 2014

Keywords:
Line tension
Surface tension
Stress tensor
Dispersion forces
Nano-slit

ABSTRACT

This is the first direct calculation of line tension at a curved edge of a solid. As an example, we consider an empty slit between two unconstrained coaxial cylinders with dispersion forces at nanoscale. The computational scheme includes the calculation of (a) the local stress tensor field inside the slit, (b) local thermodynamic surface tension as a function of the location on the slit walls, and (c) line tension at the circular rim as a function of the cylinder radius. The calculations have been made on the basis of the Irving–Kirkwood stress tensor of statistical mechanics.

1. Introduction

The concept of line tension is rooted in Gibbs' formulation of the classical theory of capillarity. Every heterogeneous system includes interfacial surfaces, which can intersect each other to form interfacial lines. Similarly as an interfacial surface possesses surface tension, an interfacial line possesses line tension. Depending on the physical configuration of a system, there are several types of line tension. So, first of all, we have to explain what kind of line tension is under consideration. Following the general classification of line tension [1] (see also surveys [2,3] for solid surfaces), we will investigate thermodynamic line tension κ as the work of formation of a linear interface per unit line length. Quantity κ is a one-dimensional analog of thermodynamic surface tension (designated as σ by Gibbs). By definition, σ is the work of disjoining two pieces of a solid (divided by a plane) from the intermolecular distance δ to infinity in a vacuum (the cleavage work):

$$2\sigma = \int_{\delta}^{\infty} f(H)dH, \tag{1}$$

where H is the width of a slit between the pieces and $f(H)$ is the cohesive force per unit area. The notion of line tension appears as a result of a change in surface tension when approaching an edge along the surface at the nano-scale. If σ is the surface tension value far from the edge and $\sigma(x)$ is a function showing the dependence

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http://dx.doi.org/10.1016/j.colsurfa.2014.02.019
0927-7757/

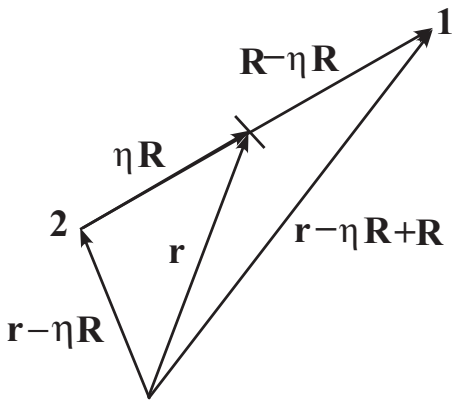

Fig. 1. Scheme of vectors standing in Eq. (3): vector **r** points the elementary unit area where the local stress tensor is sought for; the pair of interacting (through this init area) molecules are located at points 1 and 2.

of surface tension on the distance x from the edge, the line tension at the edge is

$$\kappa \equiv \frac{1}{L}\sum \int [\sigma(x) - \sigma]\, dA, \tag{2}$$

where L is the edge length and A is the surface area, the integration is carried out over each surface and summation over all surfaces meeting at the edge.

As is seen from Eqs. (1) and (2), the knowledge of cohesive force $f(H)$ is necessary for calculating both surface and line tensions. At every location and especially near the edge when σ is replaced by $\sigma(x)$, we may define $f(H, x)$ as a local value of the normal component $E_N(x)$ of the stress tensor at the slit surface. The local stress tensor was introduced in statistical mechanics by Irving and Kirkwood [4]. Working with a vacuum in a slit, the full Irving–Kirkwood stress tensor is reduced to its cohesive part of the form

$$\mathrm{E}(\mathbf{r}) = \frac{1}{2}\sum_{i,j} \int \frac{\mathbf{R}\times\mathbf{R}}{R}\, \Phi'_{ij}(R) d\mathbf{R} \int_0^1 \rho_{ij}^{(2)}(\mathbf{r} - \eta\mathbf{R}, r - \eta\mathbf{R} + \mathbf{R}) d\eta, \tag{3}$$

where **R** is the vector connecting two interacting particles with separation R between them and passing through point **r** (writing **R**×**R** symbolizes a direct vector product, which is a tensor); $\phi'_{ij}(R)$ is the derivative of the pair interaction potential $\Phi_{ij}(R)$ for particles of sorts i and j (i.e. the force of interaction between the particles); $d\mathbf{R}$ is the product of Cartesian components dR_x, dR_y, and dR_z; R is the modulus of vector **R**; $\rho_{ij}^{(2)}(\mathbf{r} - \eta\mathbf{R}, \mathbf{r} - \eta\mathbf{R} + \mathbf{R})$ is the two-particle distribution function for the particles simultaneously located at the points $\mathbf{r} - \eta\mathbf{R}$ and $\mathbf{r} - \eta\mathbf{R} + \mathbf{R}$ on the opposite sides from a unit surface with coordinate **r** (that is controlled by an additional variable η). The integration with respect to **R** is performed over the whole space. The computational scheme of the Irving–Kirkwood tensor accounts only for those molecular pairs whose connecting lines intersect the elementary unit area with coordinate **r** (which splits R into fractions η and $1 - \eta$, Fig. 1). The summation is carried out with respect to particle sorts (in a multicomponent system) and will be not needed for our calculations. After multiple use, the Irving–Kirkwood stress tensor has confirmed its physical significance. In particular, it correctly corresponds to the mechanical equilibrium condition

$$\nabla \cdot \mathrm{E}(\mathbf{r}) = 0. \tag{4}$$

A pair potential is an important element of the Irving–Kirkwood stress tensor. Among various types of forces and numerous calculations made, most attention was primary paid to attractive dispersion forces [5,6], which remain better studied in modern science. For dispersion forces without retardation, the pair potential of molecular interaction is

$$\Phi_{ij}(R) = -A_{ij}R^{-6}, \tag{5}$$

where A_{ij} is the interaction constant and R is a distance between interacting molecules of sorts i and j. In our calculations, we assume Eq. (5) to be valid down to $R = \delta$, which attaches a certain model form to the pair potential $\Phi_{ij}(R)$.

We now can formulate a computational scheme for line tension. The first stage is calculation of the local normal stress in an empty nano-slit with the aid of the Irving–Kirkwood stress tensor (3). The second stage is calculation of the local surface tension by using Eq. (1). The third stage includes the estimation of line tension according to Eq. (2). Concerning the first stage, similar calculations undertaken in the past typically referred to infinite slits (see, e.g., Ref. [6]). Only recently the results for semi-infinite slit [7,8] yielded some output to the line tension of a rectilinear crystal edge [9,10]. This paper presents the first attempt to perform calculations for a slit restricted not only in thickness, but also in all lateral directions and to estimate the line tension of a curved edge as a function of the curvature radius. The object for consideration will be an empty circular slit between two unconstrained coaxial cylinders of same radius (but, generally, of different nature). A system of such configuration and also with the van-der-Waals interaction was recently investigated by Jaiswal and Beaudoin [11], but only with respect to the integral interaction as a generalization of Hamaker's classical approach [12]. By contrast, our method yields a more detailed picture of distribution of the stress tensor and surface tension over the slit surfaces, which makes possible calculating line tension at the lateral slit rims. A similar detailed investigation, but with respect to local disjoining pressure, was recently done for the slit between an infinite plane and a cylindrical body normally oriented to the plane [13].

2. The local cohesive force

Let us detail the first stage of the above computational scheme. The system configuration is shown in Fig. 2 where a is the slit radius and H is the slit width. Since only a and H are nano-scaled parameters, we may set the cylindrical bodies to be infinite in length. We specify the point under consideration (where the stress tensor is sought-for) on the lower slit wall as the origin of cylindrical coordinates ρ, φ, z with the z-axis directed above normally to the slit walls. The positions of two interacting molecules in bodies 1 and 2 are given by vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. Evidently, these vectors are directed oppositely, but are collinear since the straight line segment of length R connecting the two interacting molecules should pass through the point under consideration (Fig. 2). We then can write

$$\mathbf{r}_1 = (1 - \eta)\mathbf{R}, \quad \mathbf{r}_2 = -\eta\mathbf{R}, \tag{6}$$

so that $\mathbf{R} = \mathbf{r}_1 - \mathbf{r}_2$.

Eq. (3) contains the integration with respect to R_x, R_y, R_z, and η. We change the variables for ρ_1, φ_1, z_1 (the components of vector $\mathbf{r}_1$) and z_2 (the z-component of vector $\mathbf{r}_2$). The Jacobian modulus for this transformation is

$$\left|\frac{D(R_x, R_y, R_z.\eta)}{D(\rho_1, \varphi_1, z_1, z_2)}\right| = \frac{\rho_1(z_1 - z_2)}{z_1^2}.$$

It also follows from Eq. (6)

$$\mathbf{R} = \mathbf{r}_1\frac{z_1 - z_2}{z_1}, \quad R = r_1\frac{z_1 - z_2}{z_1}, \tag{7}$$