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Some new mesoscopic crossover length scales concerning the Hamaker constant

ZHAO YaPu[1,2*]

[1] *State Key Laboratory of Nonlinear Mechanics (LNM), Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China;*
[2] *School of Engineering Science, University of Chinese Academy of Sciences, Beijing 100049, China*

The last three decades have witnessed a global surge in nano- and micro-mechanics driven by the rapid development of nanotechnology, microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) [1]. Although a generally accepted framework is still lacking for mesoscopic mechanics, four broad categories of viewpoints have been agreed upon [2]:

(1) Continuum mechanics works quite well even for a few atoms in diameter. In 1997, Richard E. Smalley (1943−2005), the late Nobel laureate, and Yakobson [3] once commented: "The behavior of the hollow tubules is complex, but still predictable with continuum-elastic methods. In its applications to nanotubes, the correspondence between the elastic model and molecular dynamics is remarkable. The laws of continuum mechanics are amazingly robust and allow one to treat even intrinsically discrete objects only a few atoms in diameter."

(2) The classical continuum mechanics is modifiable by surface or interface terms due to huge surface-to-volume ratios [4]. It keeps working when the surface or interface terms such as van der Waals (vdW) and Casimir interactions are introduced [5–11].

(3) The quasi-continuum method is based on the bottom-up method [12,13].

(4) The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus, Michael Levitt and Arieh Warshel "for the development of multiscale models for complex chemical systems". The QM/MM hybrid method has been widely used as a typical multiscale in mechanical systems [14,15].

Kallmann and Willstaetter [16] ascribed the mutual attraction between particles to the vdW-London forces in 1932. They made use of the additivity of the atomic interaction energies, which were proposed shortly before by Fritz Wolfgang London (1900–1954), to calculate the attraction between particles, but only for very large separations (for the purpose of the point approximation) while disregarding the medium. Bradley published a calculation for spheres and arbitrary power laws of attraction in 1932 [17], which used symbol A for the material constant but contained some mistakes. Sparnaay [18] claimed that Sir Isaac Newton (1643–1727) had already made similar calculations.

In 1936, Jan Hendrik de Boer (1899–1971) considered the role of vdW forces in material cohesion and correctly calculated the interaction of flat slabs [19]. Just one year later, Hugo Christiaan Hamaker (1905–1993) published a heavily cited paper in *Physica* [20] on the double three-dimensional integration required in evaluating the London dispersive interaction between two spheres of arbitrary radii and distances, including the planes when the sphere radius approaches infinity and a general discussion of the role of the medium. The interaction energy obtained by the above integration is highly condensed into an expression consisting of two factors, i.e., a geometric factor depending on the size, shape, and separation of the bodies involved, and a material factor depending only on the material properties—the "constant" A. Thus the Hamaker constant with a dimension

*Corresponding author (email: yzhao@imech.ac.cn)

of energy was born, and this constant A of the order of $(0.4$–$4)\times10^{-19}$ J can serve as the landmark energy to cross from continuum mechanics to mesoscopic mechanics.

Nowadays, instead of summing the effects of atoms, the absorption spectra are used to directly calculate the interaction between electromagnetic fluctuations in the bodies. This leads to a more reliable value of constant A; nevertheless, in the first-order approximation, the geometric factor remains unchanged.

The importance of Hamaker's formulation is evident in the modern designation of A as the "Hamaker constant" as approved by the International Union of Pure and Applied Chemistry (IUPAC) [21] on July 23, 1971.

In 2019, we utilized the bottom-up method to study the peeling processes of a heterostructure bonded by the vdW force, the graphene/MoS$_2$ bilayer structure as illustrated in Figure 1. Firstly, some fundamental parameters such as lattice mismatch, strain energy densities and potential between graphene and MoS$_2$ were obtained from density functional theory calculations with dispersion corrections (DFT-D2) [22]. Secondly, the peeling process was investigated subjected to various kinds of loadings by using molecular dynamics simulations. The changes in the total energy, elastic energy, vdW interaction potential and peeling force were obtained, and then the peeling forces obtained from these simulation results were compared with those from classical continuum methods. Thirdly, a mechanistic analysis of the peeling process was conducted and a quasi-continuum method was developed to describe the evolution of the peeling force. Finally, a new characteristic length, a crucial parameter that reflects the bending and interfacial properties of layered materials during peeling, was suggested by using the Hamaker constant. This study may assist in understanding the atomic-level mechanisms during the peeling of layered materials, and such mechanisms may provide some new insights into the automatic mechanical assembly of the vdW heterostructures by robots [23,24].

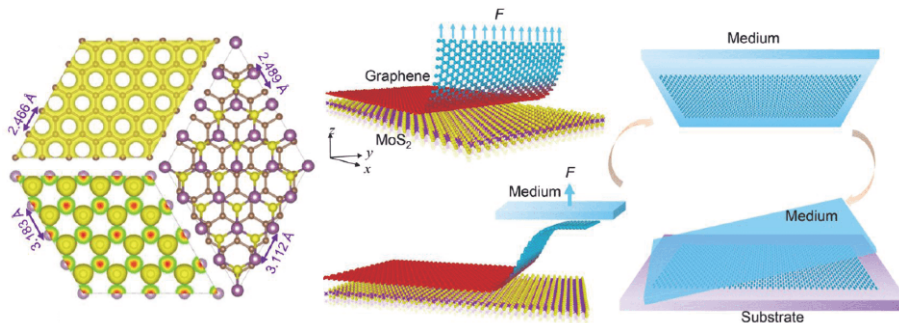Table 1 shows how the vdW interactions compete with

Figure 1 (Color online) Mechanical peeling of graphene/MoS$_2$ vdW heterostructures [22].

Table 1 Some characteristic length scales related to the Hamaker constant A

Length scale	Formula	Physical interpretation
Thickness of precursor film (by de Gennes)	$a_p = \sqrt{\dfrac{A}{6\pi\gamma_{lv}}}$	Competition between the vdW interaction and capillarity. Typical thickness of precursor film is of the order several Å. γ_{lv}– liquid-vapor surface tension
Length of precursor film (by de Gennes)	$L_p = \dfrac{1}{Ca}\sqrt{\dfrac{SA}{6\pi\gamma_{lv}^2}}$	Competitions among spreading inertia, spreading parameter and vdW interactions. S– spreading parameter, Ca– capillary number
Mesh size	$\xi \sim \sqrt[3]{\dfrac{A}{E}} \sim \sqrt[3]{\dfrac{A}{G}}$	Competition between the vdW and elastic deformation energies
Detachment length of cantilever (by the author) [25]	$L_{\text{detach}} = C\times g\sqrt[4]{\dfrac{Et^3}{A}}$	Bending of cantilever under the action of the vdW force. Adhesion/stiction occurs when the cantilever length is longer than this length
Peeling length (by the author) [22]	$L_{\text{peeling}} = 4\sigma_0\sqrt{\dfrac{2\pi D}{A}}$	$D = \dfrac{Eh^3}{12(1-v^2)}$ – bending rigidity of plate, σ_0– atom equilibrium distance
Bending length (by the author)	$l_{\text{bending}} = \dfrac{EI}{A}$	Beam bending under the action of the vdW force. EI– bending rigidity of beam. Some typical scales for the single-walled carbon nanotubes are presented in Table 2
Electrostatic length (by the author)	$l_{\text{electric}} = \dfrac{e^2}{4\pi\varepsilon_r\varepsilon_0 A}$	Competition between electrostatic and vdW interactions
Impact length (by the author)	$l_{\text{impact}} = \sqrt[3]{\dfrac{A}{6\pi\rho V^2}}$	Competition between the vdW interactions and impact inertia ρV^2

Table 2 Length scales for single-walled carbon nanotube with different diameter D

D (nm)	l_{min} (nm)	l_{max} (nm)
1	0.293	2.93
2	2.63	26.3
3	9.21	92.1
4	22.26	222.6
5	43.97	439.7
6	76.55	765.5

capillarity, elastic deformation, electrostatic interaction and impact inertia. Some characteristic scales are summarized and some new length scales are suggested by the author for the first time. These length scales will play vital roles when they are comparable with the characteristic length of the system in study.

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