Theory of dispersion forces and its application to molecular assemblies on a crystalline surface

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Outline

vdW forces for pedestrians

How does the van der Waals force work?

- pairwise summation method
- Casimir force
- fluctuation-dissipation theorem

V. A. Parsegian, *van der Waals Forces* (2006)

van der Waals forces everywhere

- bio-physics, chemistry: interfacial and cohesion energies
- soft-condensed matter physics: physical adsorption
- nano-science: molecular modeling; graphite binding

Theoretical Approach

1. density-functional theory; tight-binding method; RPA.
2. Lifshitz's theory of dispersion forces.
3. polymer dynamics (Brownian motion).

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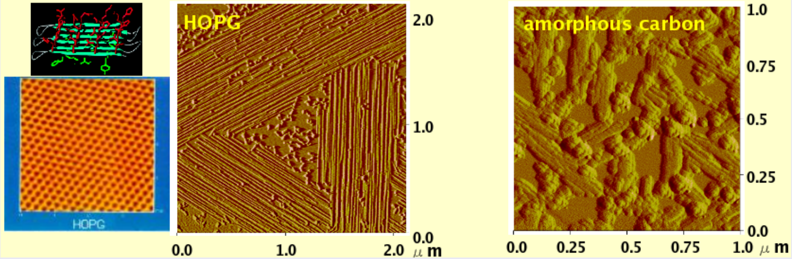
Oriented-patterned formation

Template-directed molecular self-assemblies

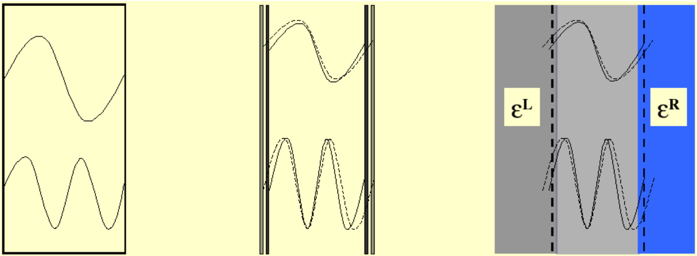


Phys. Rev. Lett. **96**, 18301 (2006)

Outline

Lifshitz theory

From Planck, Casimir, to Lifshitz.

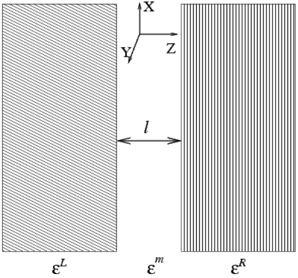


- Hamaker coefficient A_H:

$$E = -\frac{A_H}{12\pi\ell^2}$$

Calculation of free energy between two slabs

- for mode ω_j, $F_j = -k_B T \ln Z_j$; $Z_j = \sum_n \exp\left[-(n+\frac{1}{2})\frac{\hbar\omega_j}{k_B T}\right]$

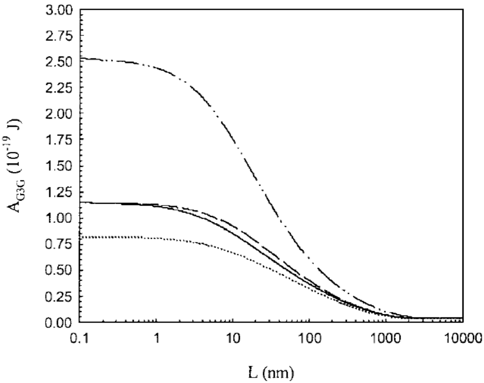


- solve $\nabla \cdot \vec{D} = ik_x D_x + ik_y D_y + \frac{\partial D_z}{\partial z} = 0$; $\vec{D} = \epsilon \vec{E}$

$$A_H = -\frac{3\ell^2 k_B T}{\pi} \sum_{\omega_j, \vec{k}} \ln\left[1 - \left(\frac{\epsilon_L(\omega,\vec{k})-1}{\epsilon_m(\omega,\vec{k})+1}\right)\left(\frac{\epsilon_R(\omega,\vec{k})-1}{\epsilon_m(\omega,\vec{k})+1}\right) e^{-2k\ell}\right]$$

Hamaker coefficient between two graphite slabs

Hamaker coefficient is constant within non-retarded regime.



Dagastine *et al.*, J. Colloid Interface Sci. **249**, 78 (2002)

Spatial dispersions in the dielectric function

Bringing spatial dispersions to the theory of vdW forces $\epsilon(\omega, \vec{k})$

- $\mathbf{D}(\omega, \vec{r}) = \int \epsilon(\omega, \vec{r}, \vec{r}')\mathbf{E}(\omega, \vec{r}')d\vec{r}'$
- Characteristic length dictates if k can be taken as $k \approx 0$.

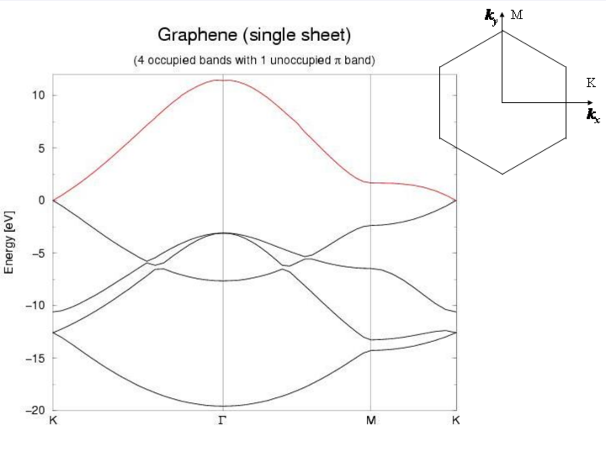
Bringing spatial dispersions to the theory of vdW forces

- at larger (finite) wavevectors $\vec{k}$, the screening is not as effective as at $\vec{k} \to 0$.
- non-retarded Hamaker constant is separation dependent.

Phys. Rev. B **71**, 235412 (2005).

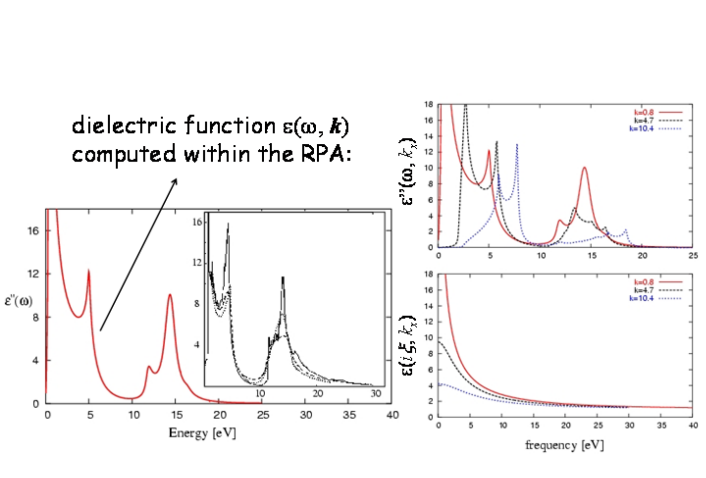
Numerical example: graphite

Band structure



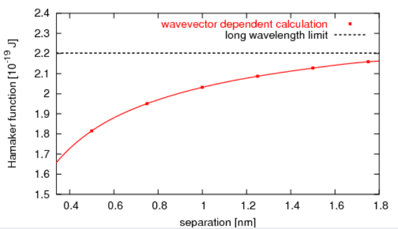
Dielectric screening of graphite

Dielectric function $\epsilon(\omega, \vec{k})$



Hamaker coefficient between two graphite slabs

Hamaker coefficient depends on separations



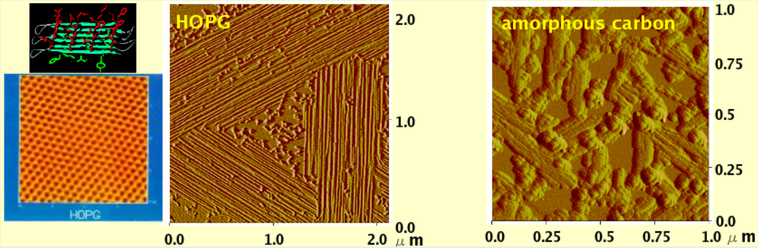
Hamaker coefficient [A_H in the unit of 10^{-19} J; ℓ in the unit of nm]

	$\ell = 0.5$	$\ell = 1.0$	$\ell \gg 1$	Expt[†]
graphite-water-graphite	0.72	0.87	0.99	0.5-1.0
graphite-air-graphite	1.82	2.03	2.20	2.1-5.9

Outline

Patterned adsorption on graphite

Example

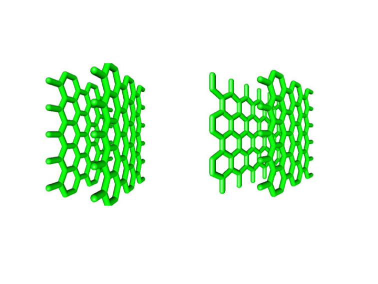


protein fibrils; micelles.

Anisotropy induced by $\epsilon(\omega, \vec{k})$

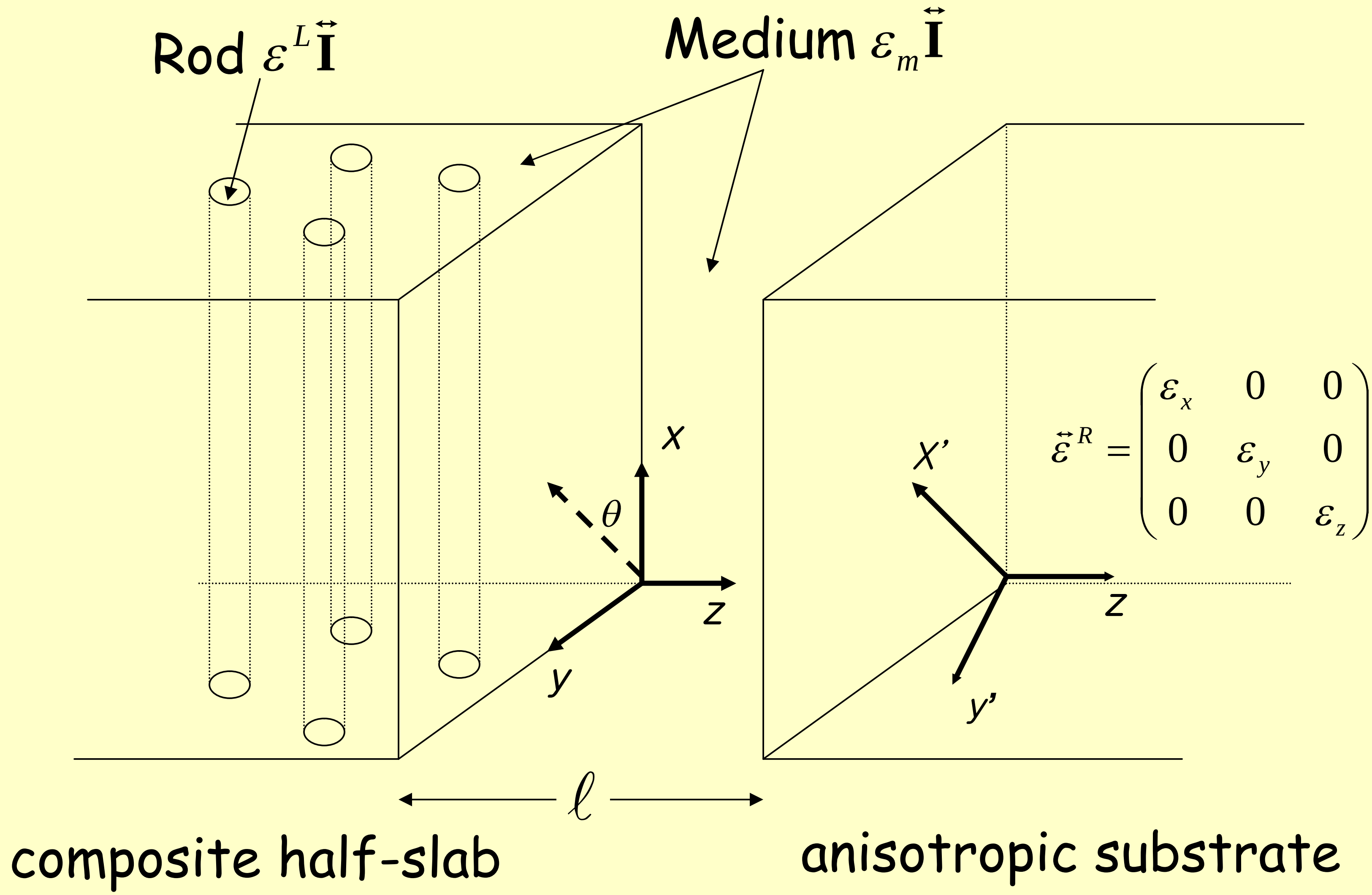
Anisotropic screening due to the directionality of $\vec{k}$

- $$\epsilon(\omega) \longrightarrow \begin{pmatrix} \epsilon(\omega, k_x) & 0 & 0 \\ 0 & \epsilon(\omega, k_y) & 0 \\ 0 & 0 & \epsilon(\omega, k_z) \end{pmatrix}$$



$\longrightarrow$ compute van der Waals binding energies for different orientations.

anisotropic vdW interaction



Analysis of the orientational ordering

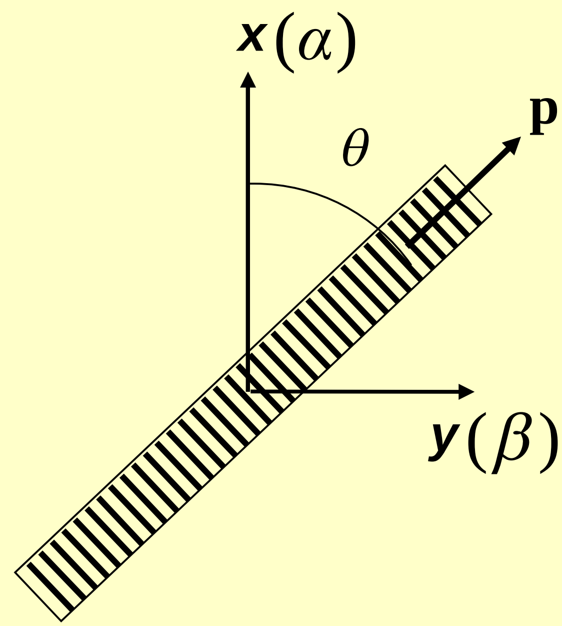
Smoluchowski equation

$$\frac{\partial \psi}{\partial t} = D_{rot}\left(\mathbf{p}\times\frac{\partial}{\partial \mathbf{p}}\right)\cdot\left[\mathbf{p}\times\frac{\partial \psi}{\partial \mathbf{p}} + \frac{\psi}{kT}\mathbf{p}\times\frac{\partial U}{\partial \mathbf{p}}\right]$$

steady-state solution

$$\frac{\partial \ln \psi}{\partial p_x} = -\frac{1}{kT}\frac{\partial U}{\partial p_x}$$

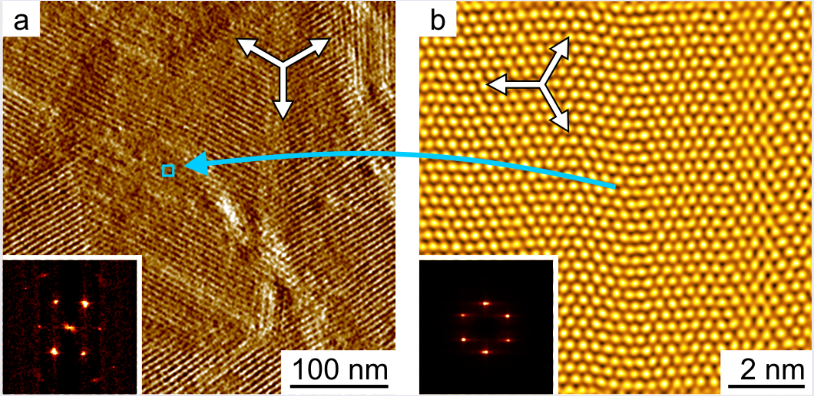
probability density function



Outline

Adsorption of micelles on a gold (111) surface

Template-directed molecular self-assembly on a gold (111) surface



Puzzle: patterned physisorption on a metallic substrate

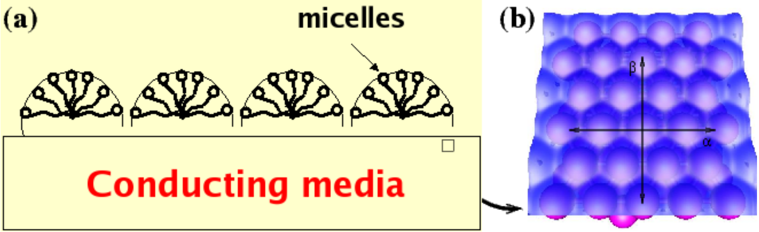
Why these do not work

image method
epitaxial principle
pairwise summation theory

anisotropic vdW force

delocalized conduction electrons
isotropic electronic screening:
$\epsilon(\omega \to 0) \longrightarrow \infty$.

Figure: (a) Micelles on a conducting substrate. (b) A gold (111) surface.



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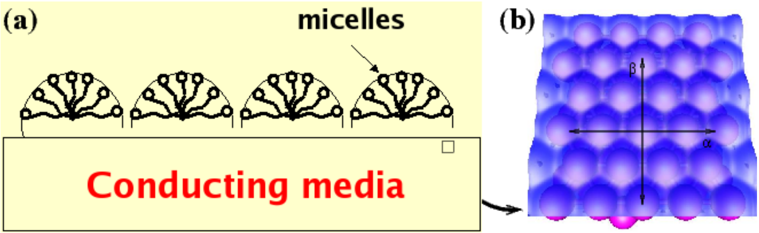


Outline

Dressed phonon in metals

Screening in metals: charge redistribution

electronic screening (plasma model)

$$\epsilon^{el}(\omega) = 1 - \frac{4\pi Ne^2/m}{\omega^2}$$

dressed phonon screening

$$\frac{1}{\epsilon(\omega, \vec{k})} = \frac{1}{\epsilon^{el}(\omega)} \frac{1}{\epsilon^{ion}_{dressed}(\omega, \vec{k})}$$

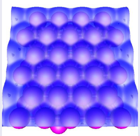
$$\begin{aligned} \epsilon^{ion}_{dressed}(\omega, \vec{k}) &= 1 - \tilde{\omega}^2(\vec{k})/\omega^2 \\ \tilde{\omega}(\vec{k}) &= c_s(\hat{k})k \end{aligned}$$

Ashcroft and Mermin, *Solid State Physics* (1976).

Sound velocity is anisotropic in metals

Within continuum mechanics,

$$c_s^2(\hat{k}) = \left(\frac{\partial p}{\partial \rho}\right)_V = \left(\frac{\partial p^{el}}{\partial \rho}\right)_V + \left(\frac{\partial p^{ion}}{\partial \rho}\right)_V$$

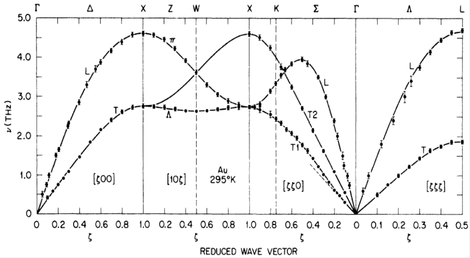


$$\left(\frac{\partial p^{el}}{\partial \rho}\right)_V = \frac{4\pi n Z e^2/M}{k_0^2}$$

Electronic part dominates, but ...

$(\partial p^{ion}/\partial \rho)_V$ is direction-dependent.

Phonon dispersion relations in gold.



Outline

Formalism: phonon-induced anisotropy in vdW forces

at $k = 0.001 \cdot 2\pi/a$, $c_s(\hat{K}) = 5273.5$ m/s, $c_s(\hat{X}) = 3921.3$ m/s:

$$\begin{aligned}\epsilon(\omega, \mathbf{k} = k\hat{K}) &= \epsilon^{el}(\omega)\left(1 - \frac{(3.4\times 10^{-3})^2}{\omega^2}\right)\\ \epsilon(\omega, \mathbf{k} = k\hat{X}) &= \epsilon^{el}(\omega)\left(1 - \frac{(2.5\times 10^{-3})^2}{\omega^2}\right).\end{aligned}$$

A_H between a rod and gold is (unit: $k_B T$)

$$\frac{3}{8\pi}{}' \int d\theta dx\, x^2 e^{-x}\left(\frac{\epsilon^{rod} - 1 - 2\Delta}{4}\cos^2\theta + \Delta\right)\left(\frac{\epsilon_z^{gold} - 1}{\epsilon_z^{gold} + 1}\right).$$

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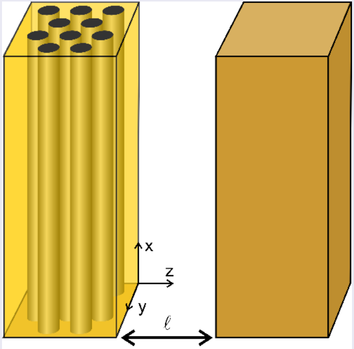
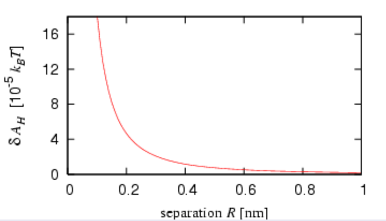
Brownian motion and all that

A semi-infinite composite slab on a gold (111) surface



Anisotropy in A_H



$$V(R) = -\frac{A_H a_m^2 \ell_m}{6R^3},$$

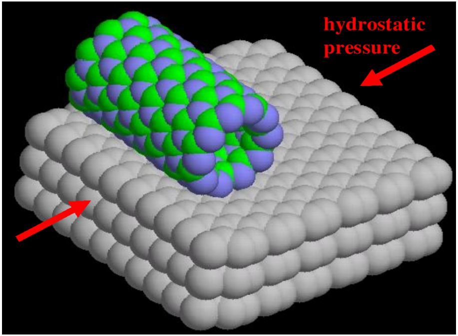
$$\delta V(R = 0.2nm) \approx 2k_B T.$$

Manipulate a CNT on a polycrystalline substrate

Incorporate phonon screening in the theory of vdW forces

1. Provide a generic mechanism.
2. $c_s(\hat{k})$ dictates the orientation.

applying an external constraint



Summary

- Spatial dispersions of $\epsilon(\omega, \vec{k})$ in the theory of vdW forces.
- Lattice vibrations can induce anisotropy in vdW forces.
- A long rod-like object should align along the slowest sound speed direction on a metal surface.

- Outlook
  - microscopic theory of vdW forces
  - apply vdW forces beyond pairwise summation in molecular simulations

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N. S. Wingreen (Molecular Biology, Princeton)
R. Car (Chemistry, Princeton)

References

van der Waals Forces; Molecular Self-Assemblies

Phys. Rev. B **71**, 235412 (2005)
Phys. Rev. Lett. **96**, 18301 (2006)
J. Phys. Chem. B **110**, 16624 (2006)
phonon-induced anisotropic vdW forces, submitted.