Theory, Modeling & Computation in Chemistry:
Its Scope and Role in Frontier Areas of Research in Chemistry-Part 2

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Bhabha Atomic Research Centre, Mumbai

Electronic structure calculations
Applications to Molecules and Hard Matter

Molecular Hydrogen Adsorption in Metal Doped Modified Carbon Based Nanomaterials

KRS Chandrakumar & SK Ghosh, Chem. Phys. Lett. 447, 208 (2007)
Nano Letters 8, 13 (2008)

KRS Chandrakumar, K Srinivasu & SK Ghosh,
J. Phys. Chem. C 112, 15670 (2008)

K Srinivasu, KRS Chandrakumar & SK Ghosh,
Phys. Chem. Chem. Phys. 10, 5832 (2008)
ChemPhysChem. 10, 427 (2009)
J. Phys. Chem. A 114, 12244 (2010)
J. Phys. Chem. C 115, 1450 (2011)

Hydrogen Economy: Major issues and problems

1. Hydrogen Economy : Needs a Visionary Strategy

2. Hydrogen - Nonpolluting and Renewable Form
   of Future Energy Sources

3. Two most Important Problems :
   - How do we generate hydrogen?
     - Water Splitting ? Solar Energy ? Catalysis ?
   - How do we store hydrogen?
     - Novel Molecules and Materials ?

What do we do ?

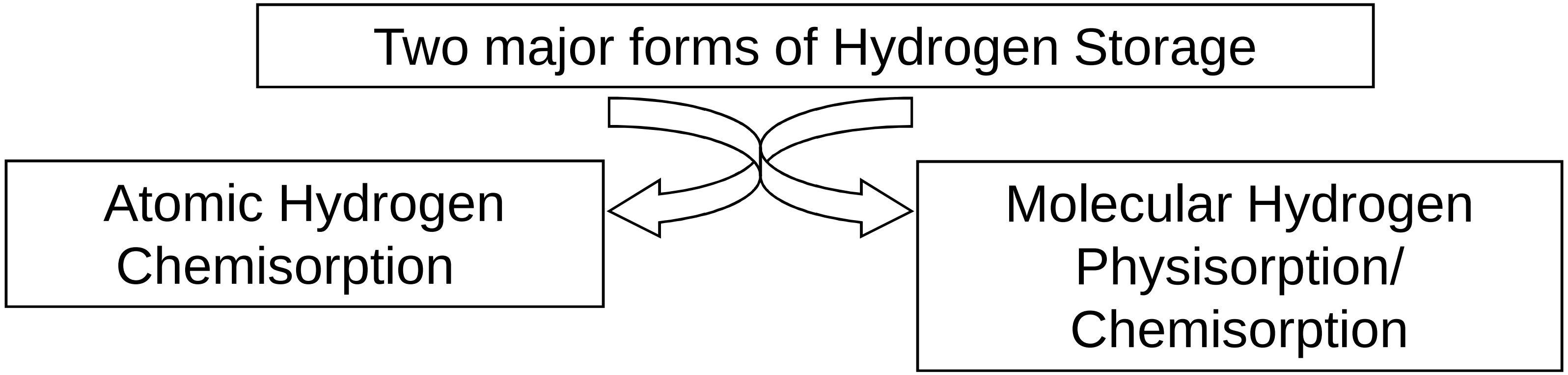
We follow the Theory and Modeling route
towards Design of Novel Molecules and Materials:

- Insight into the problems of hydrogen energy & economy
  - Catalysis for Water Splitting
  - Materials for Hydrogen Storage.

HYDROGEN STORAGE MATERIALS

1. Conventional Hydrogen Storage Materials do not yet satisfy all the criteria for efficiency & cost effectiveness

2. Major challenge : Search for a cost effective material with high hydrogen adsorption capacity with reversible hydrogen adsorption/ desorption characteristics at ambient conditions



Two major forms of Hydrogen Storage

Atomic Hydrogen
Chemisorption

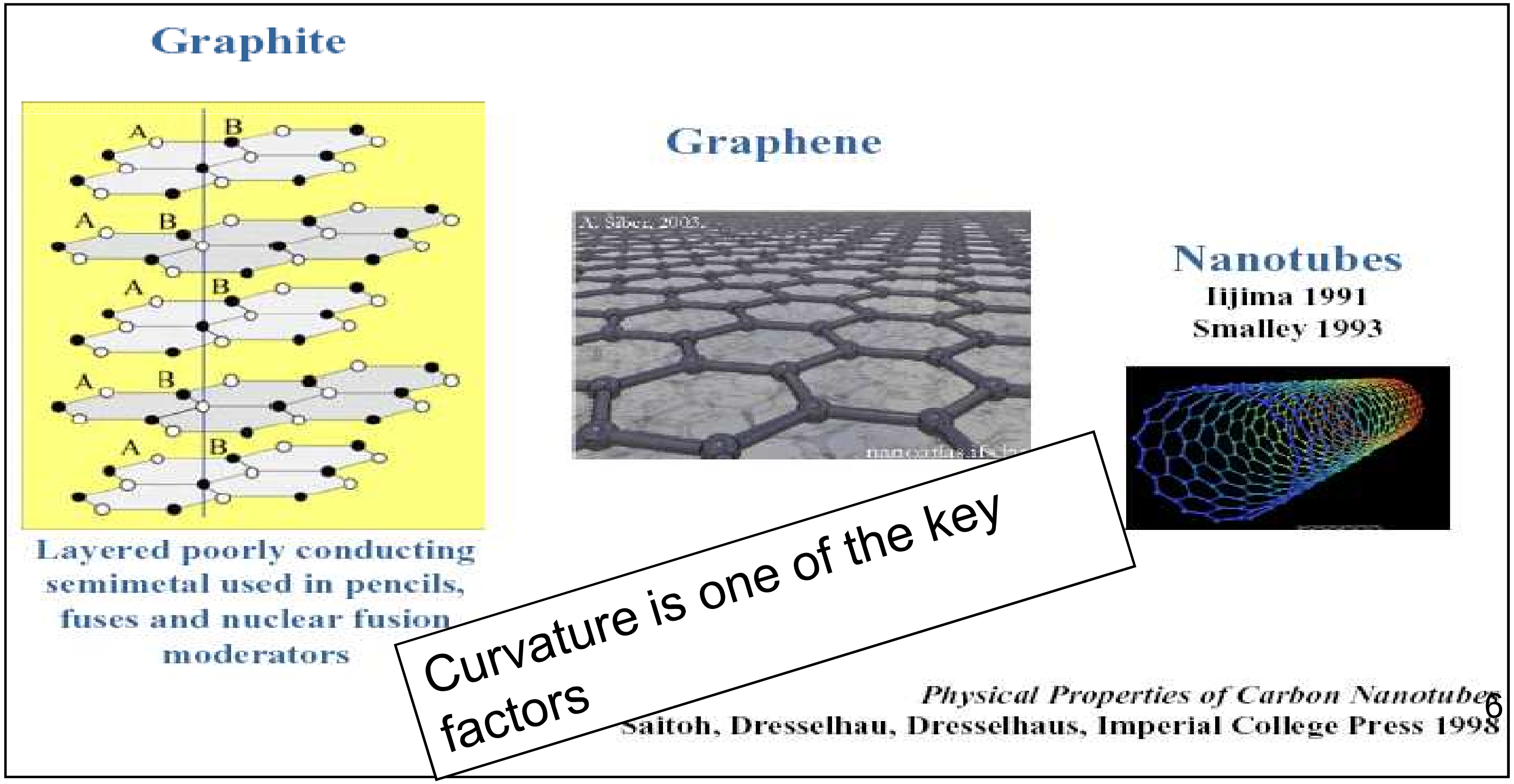
Molecular Hydrogen
Physisorption/
Chemisorption

Present work: Theory and modeling of the interaction of Molecular Hydrogen with Novel Molecules and Materials to gain basic understanding & insight into the problems for the design of efficient Hydrogen Storage Materials

Carbon based nanomaterials

Carbon nanostructured materials: Fullerenes, nanoscrolls, nanofibers, graphene, multiwall nanotubes, carbon platelets, etc.

Although the basic building unit in all these materials is carbon atom, why are their properties so different from each other?



Graphite

Layered poorly conducting semimetal used in pencils, fuses and nuclear fusion moderators

Graphene

Nanotubes
Iijima 1991
Smalley 1993

Physical Properties of Carbon Nanotubes
Saitoh, Dresselhau, Dresselhaus, Imperial College Press 1998

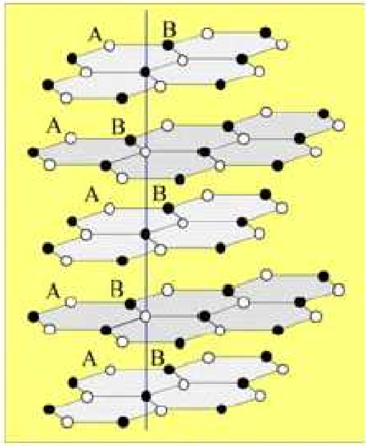
Curvature is one of the key factors

Molecules → Extended Systems

6-membered Ring as Building block for Graphite, Graphene, Nanotubes

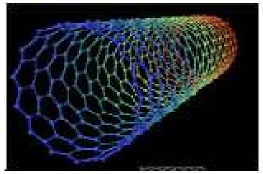
Introduction of Curvature for Nanotubes, Fullerenes
&
5-membered Ring for Fullerene

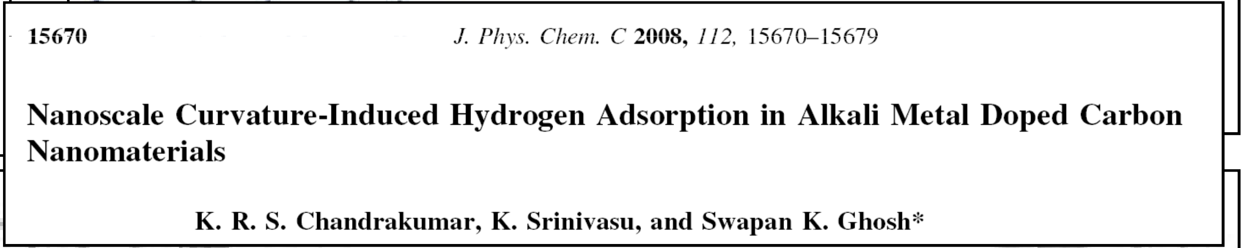
Graphite



Graphene

Nanotubes
Iijima 1991
Smalley 1993

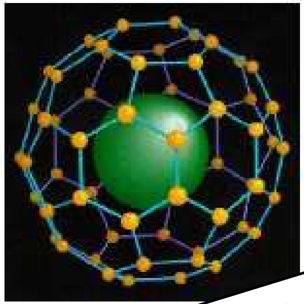




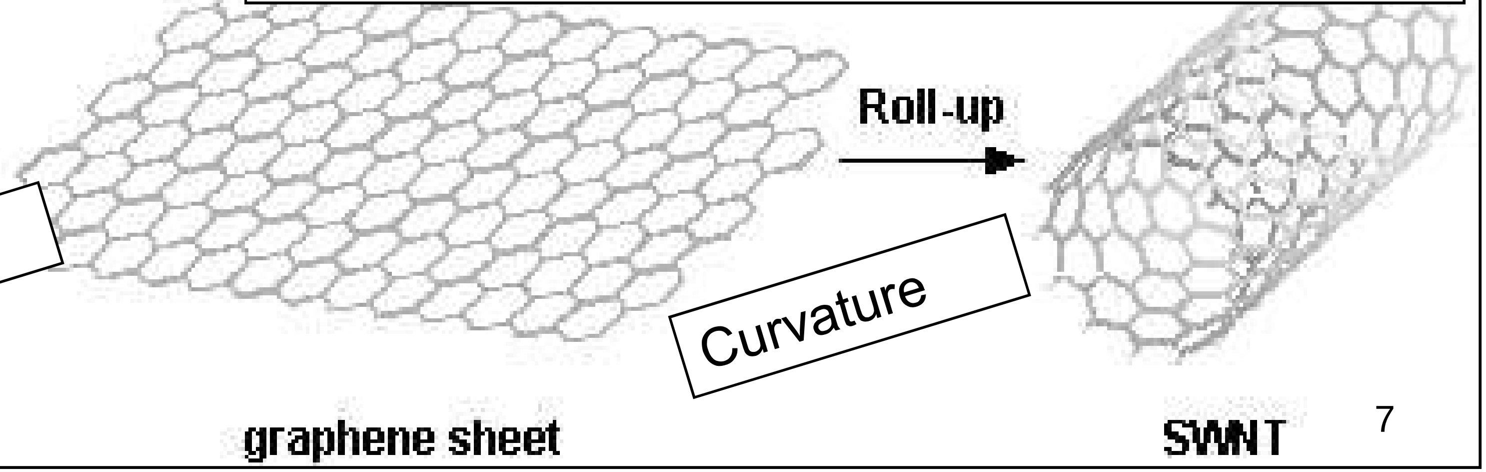
15670 *J. Phys. Chem. C* **2008,** *112,* 15670–15679

Nanoscale Curvature-Induced Hydrogen Adsorption in Alkali Metal Doped Carbon Nanomaterials

K. R. S. Chandrakumar, K. Srinivasu, and Swapan K. Ghosh*



Confinement



Curvature

Alkali-Metal-Induced Enhancement of Hydrogen Adsorption in C_{60} Fullerene: An *ab Initio* Study

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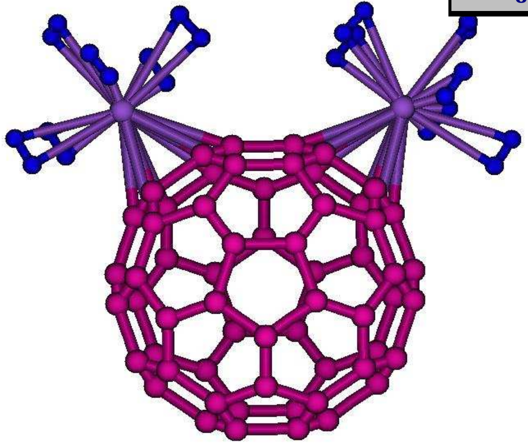
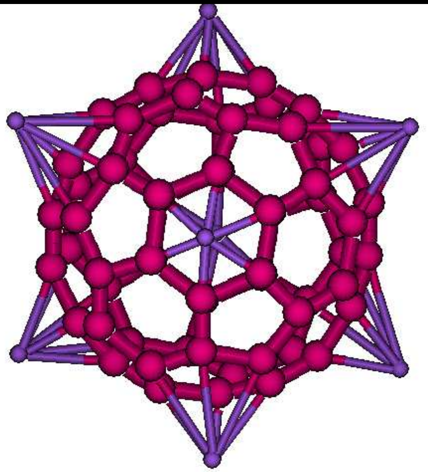
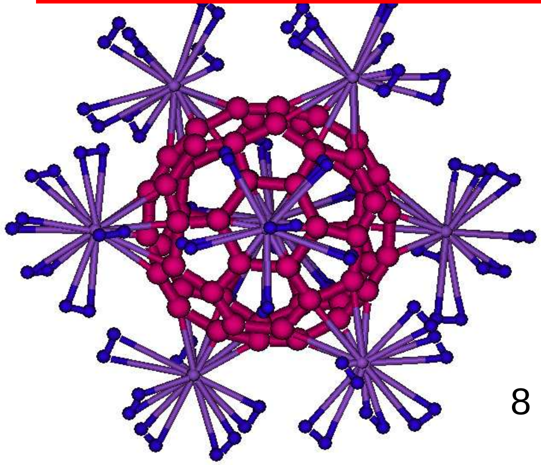
Systems	C-X Bond length	MetalC_{60} Binding energy	Charge on the metal atoms
LiC_{60}	2.268	-35.02	0.42 (0.74)
NaC_{60}	2.478	-32.61	0.55 (0.89)
KC_{60}	2.971	-32.75	0.62 (0.68)
Na_2C_{60}	2.430	-65.61	0.50 (0.86)
Na_8C_{60}	2.460	-220.93	0.35 (0.71)

Bond length M-H_2	Binding energy of H_2	Charge on the metal atoms
2.200	-5.33 (2)	0.14 (0.53)
2.581	-10.33 (6)	0.11 (0.59)
3.080	-7.24 (6)	0.62 (0.68)
2.562	-19.25 (12)	0.26 (0.57)
2.591	-97.85 (48)	0.11 (0.59)







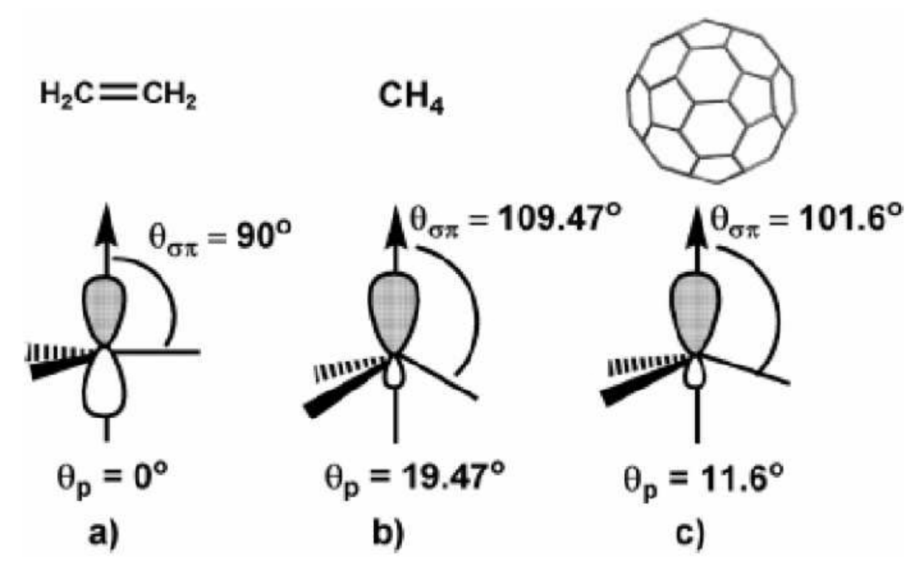
Curvature induced molecular interaction

Curvature might be an important factor behind the reactivity of fullerenes or nanotubes in comparison to graphene or graphite

- The configuration at each carbon atom in fullerenes is not planar, but slightly pyramidal in nature: consistent with some sp3 character present in the essentially sp2 carbons.

- Presence of 5-membered rings provide the curvature necessary for forming a closed cage structure.

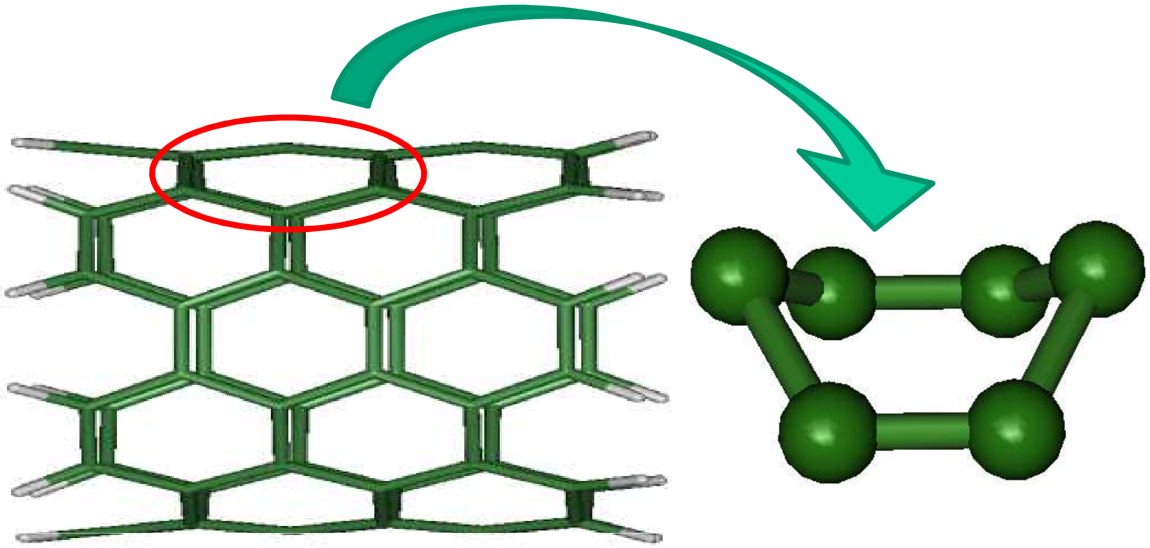
- The *sp*2-hybrized carbon atom in C_{60} is slightly pyramidal; the angle between its pπ-orbital and the σ-bonds is larger than 90° leading to formation of curved π-conjugation within the carbon surfaces of fullerenes .



Curved hexagonal or hybrid hexagon - pentagon carbon-carbon networks.

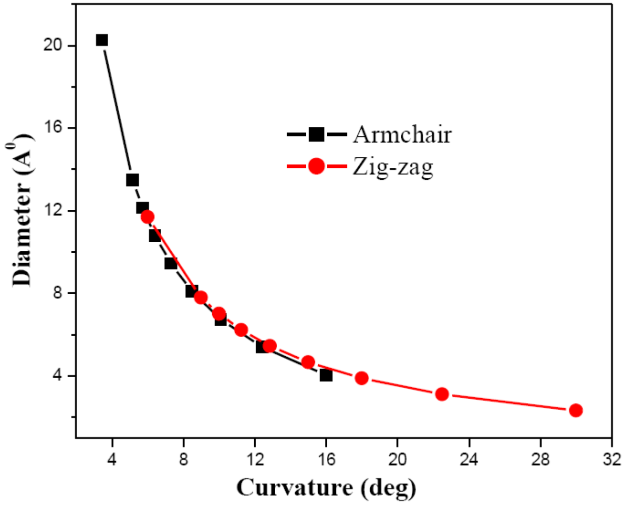
- The structural diversity in carbon based nanomaterials is predominantly due to the modifications in the electronic structure essentially driven by the degree & nature of hybridization of the valence orbitals of carbon atoms depending on structural topology & dimensionality.
- The curvature of the carbon surface plays an important role in determining the physical and chemical properties of these materials in a significant way. The effect of curvature can be as large as the effects due to the defects or vacancies created at the surface.

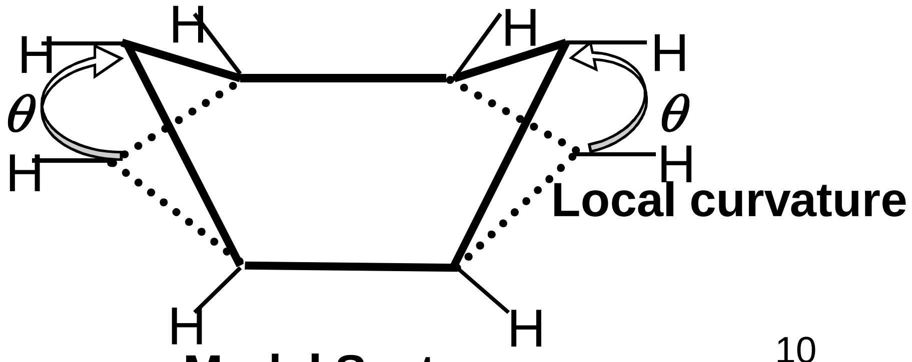
Governing Role of Nanoscale Curvature



Binding energy
not very sensitive to
- Bond distance
- Size of the fullerenes
- Number of C atoms

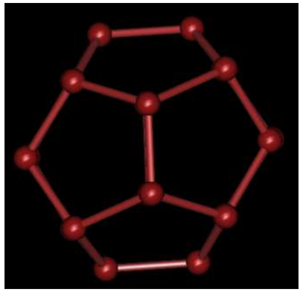
Intra-curvature: C28 > C32 > C36 > C20 > C70 > C60
Binding energy: C28 > C36 > C32 > C20 > C70 > C6



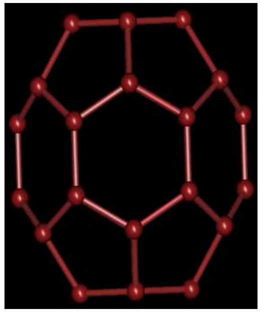


Model System

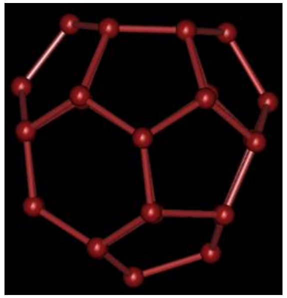
Fullerenes ----------



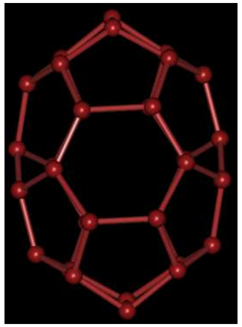
C_{20}



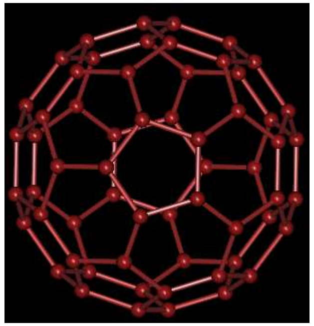
C_{36}



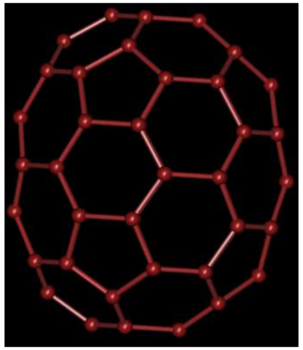
C28



C_{32}

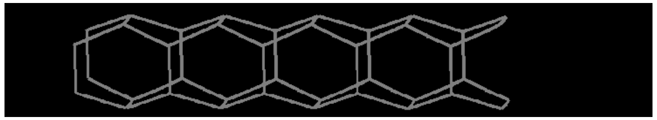


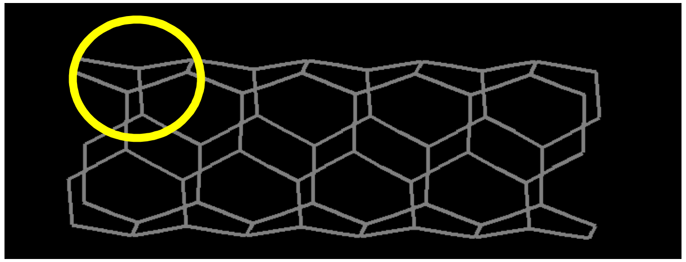
C_{60}

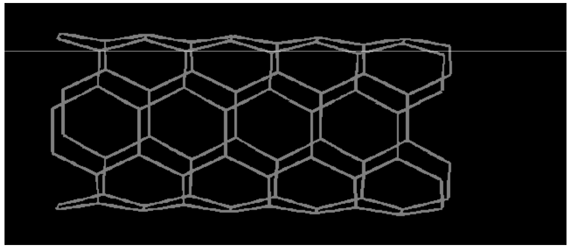


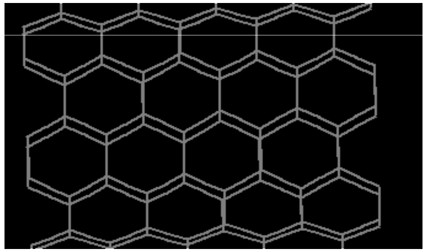
C_{70}

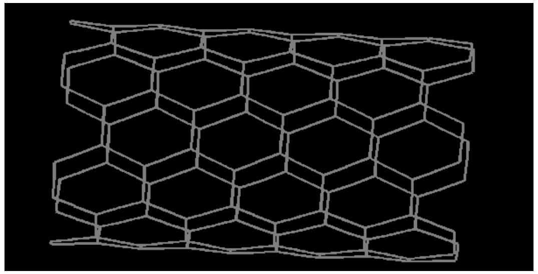
Nanotubes-----

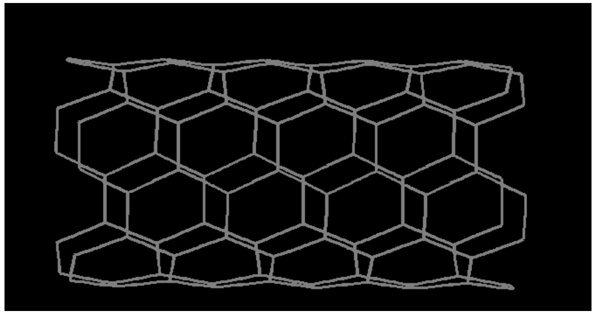


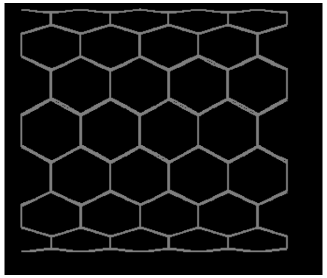


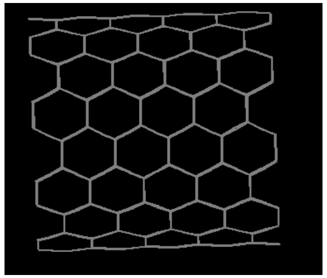






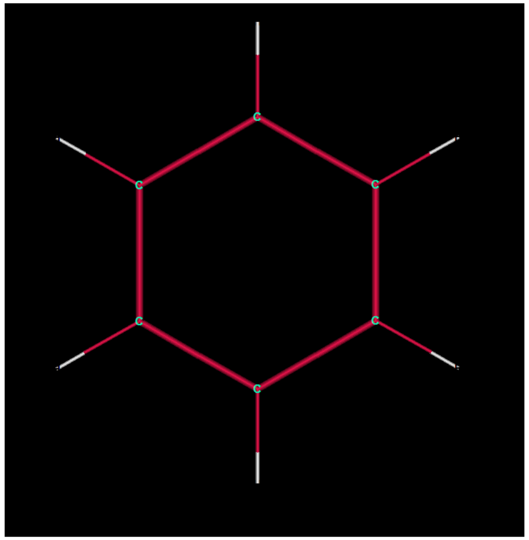




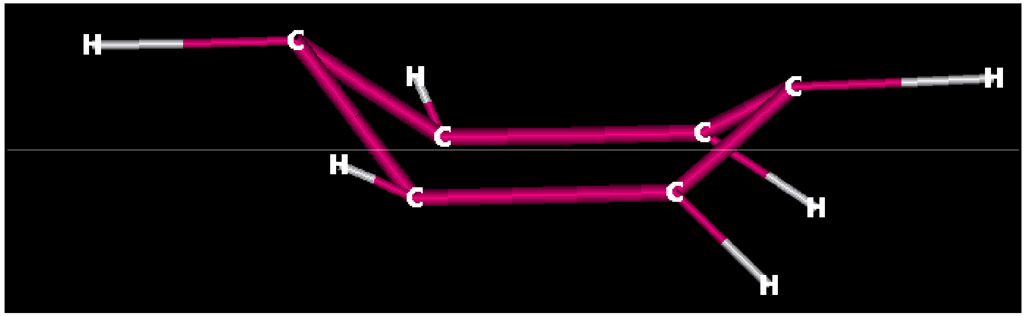


Structure of planar and curved benzene

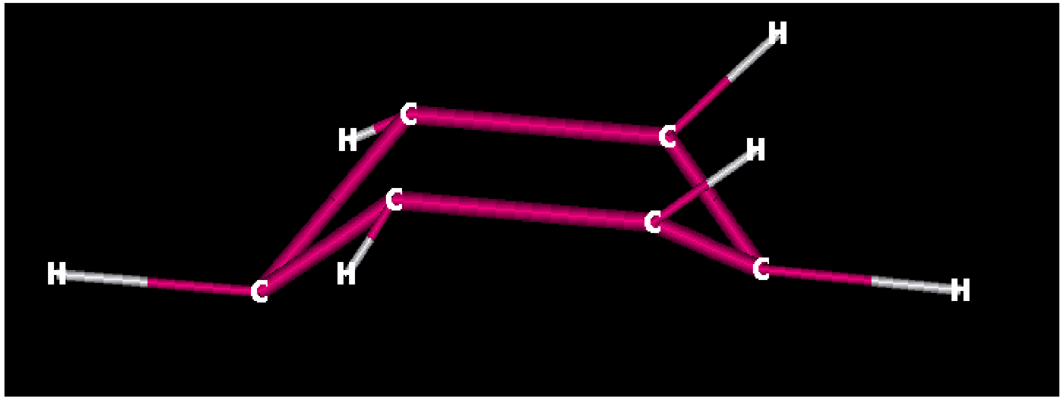
- Consider Benzene molecule as prototype system
- Create the effect of curvature artificially
- The dihedral angle is varied (0º to 35º)
- The structurally deformed benzene molecule is allowed to interact with H_2 molecule & Na atom

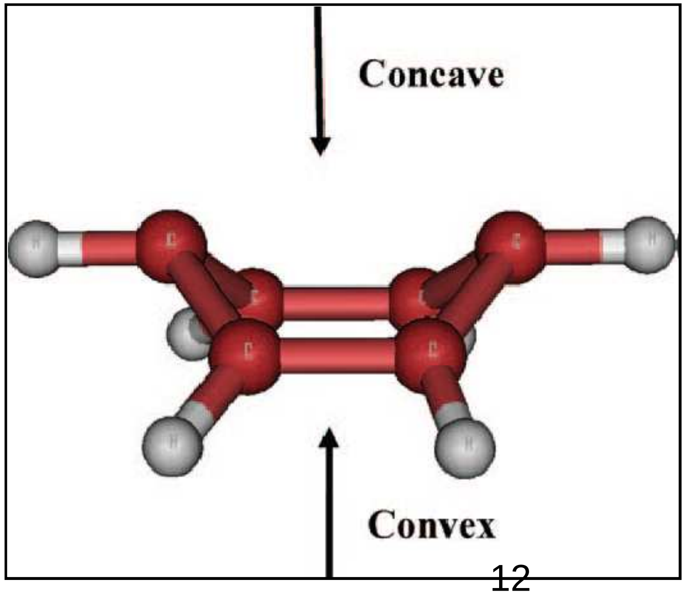


Intra-deformed Benzene-Concave



Intra-deformed Benzene-Convex





Planar and curved benzene as Model System

- Consider Benzene molecule as prototype system
- Create the effect of curvature artificially
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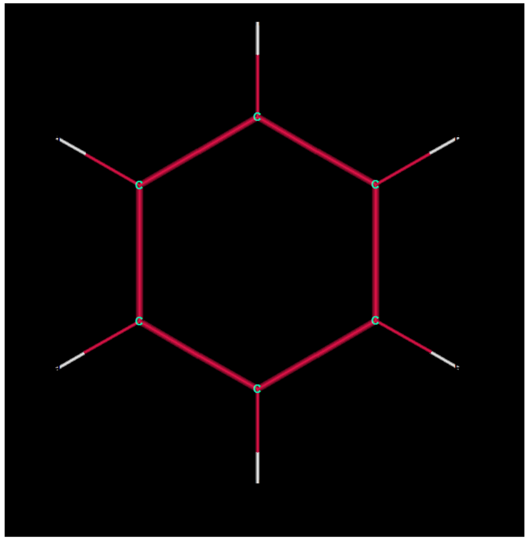
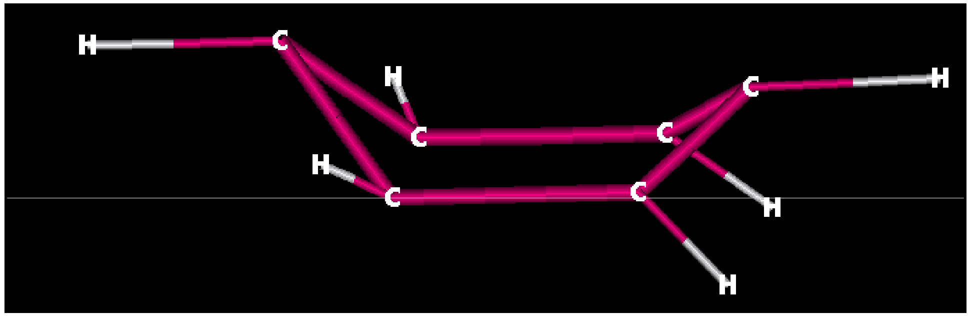
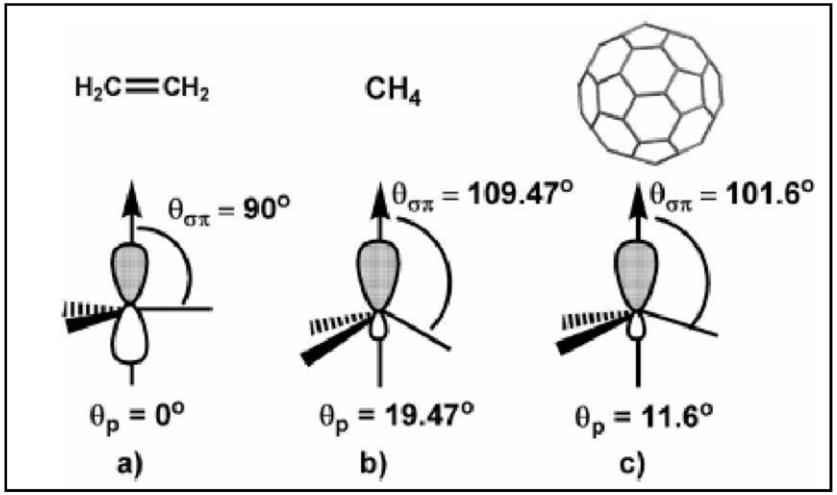


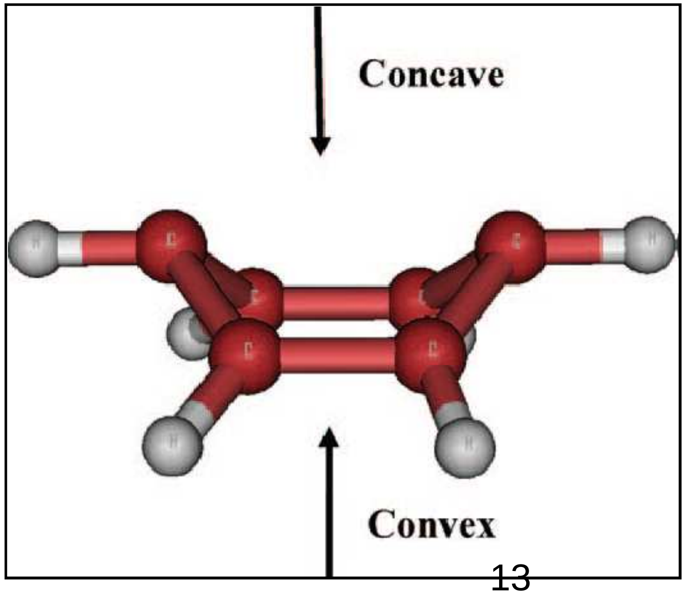


Intra-deformed Benzene

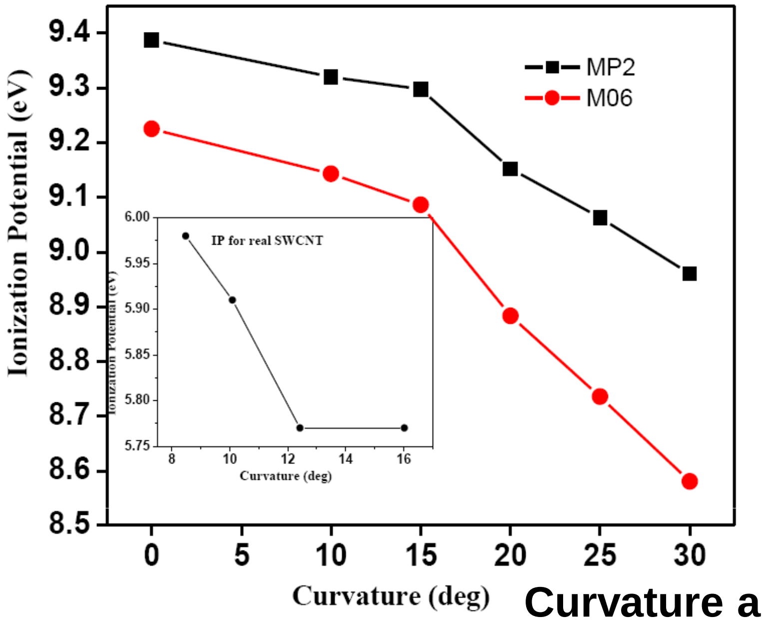
Intermediate sp3 & sp2 hybridization

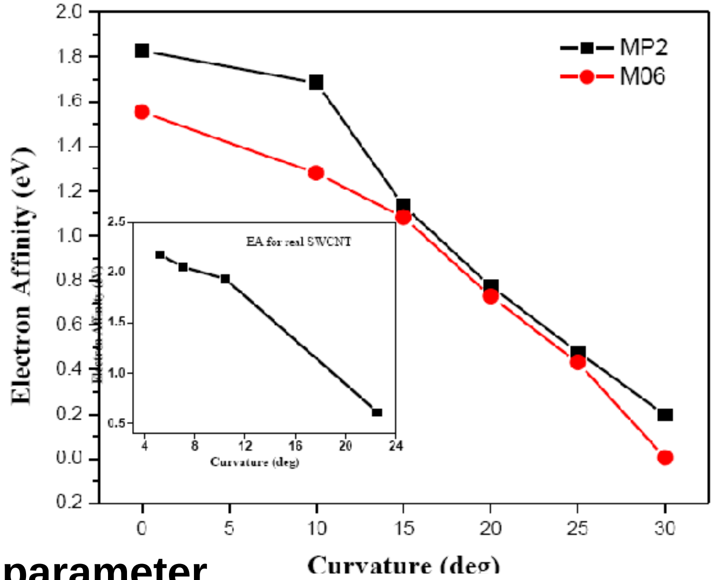


Curved hexagonal or hybrid hexagon - pentagon carbon-carbon networks.

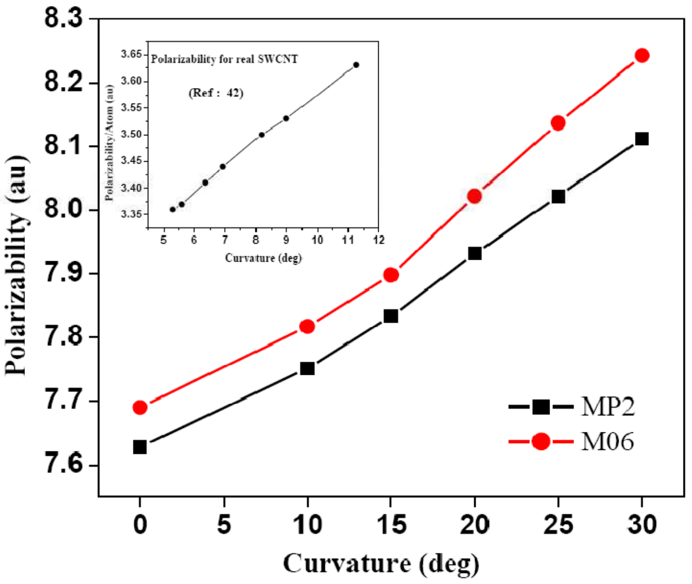


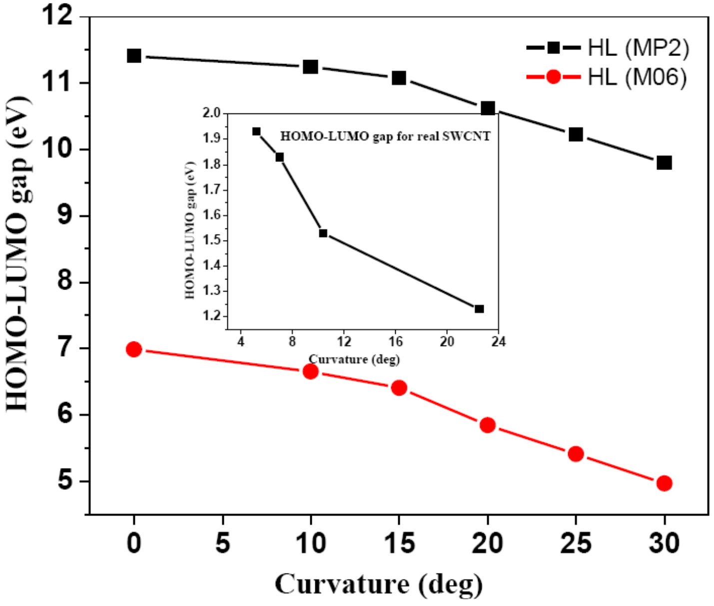
Governing Role of Nanoscale Curvature on the Electronic Properties Carbon Nanotubes





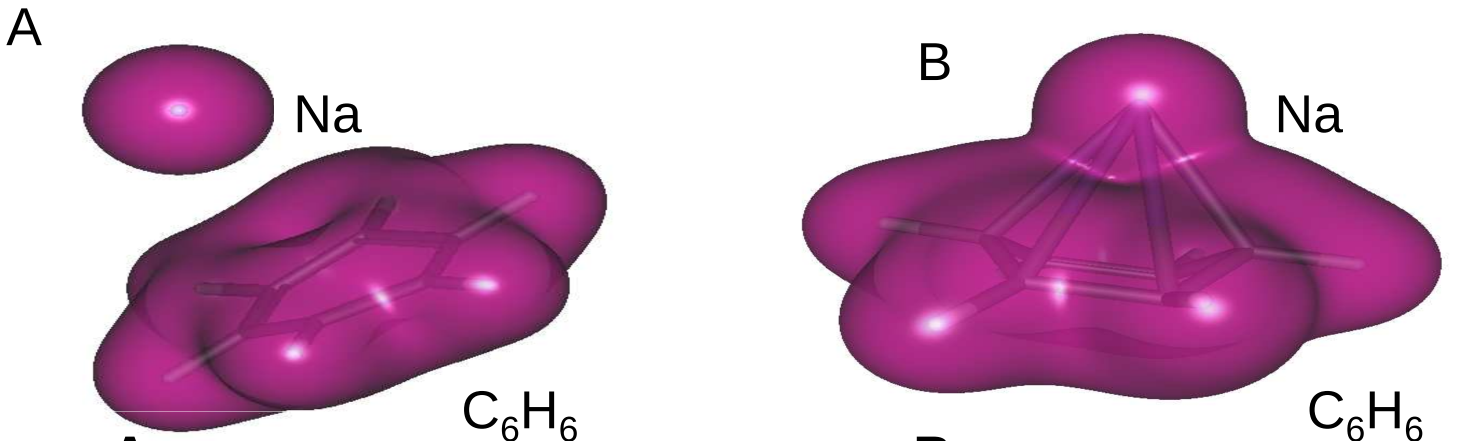
Curvature as a key parameter ...

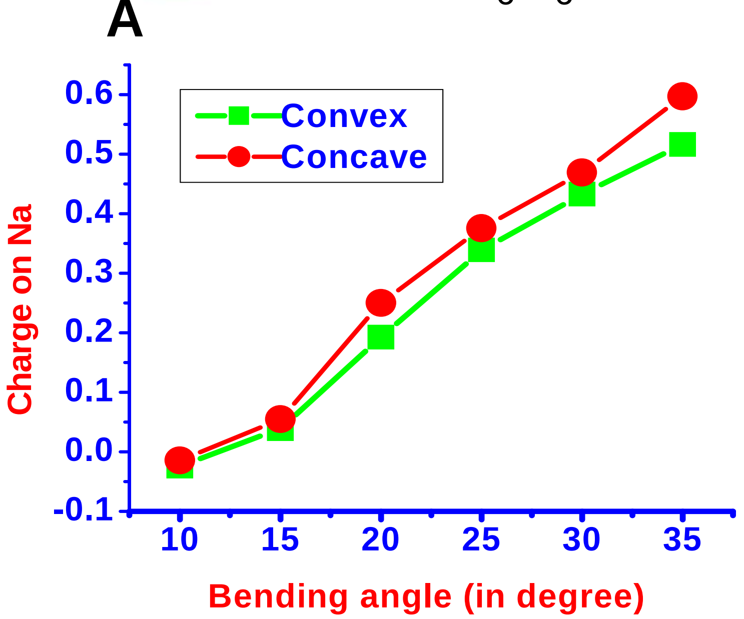


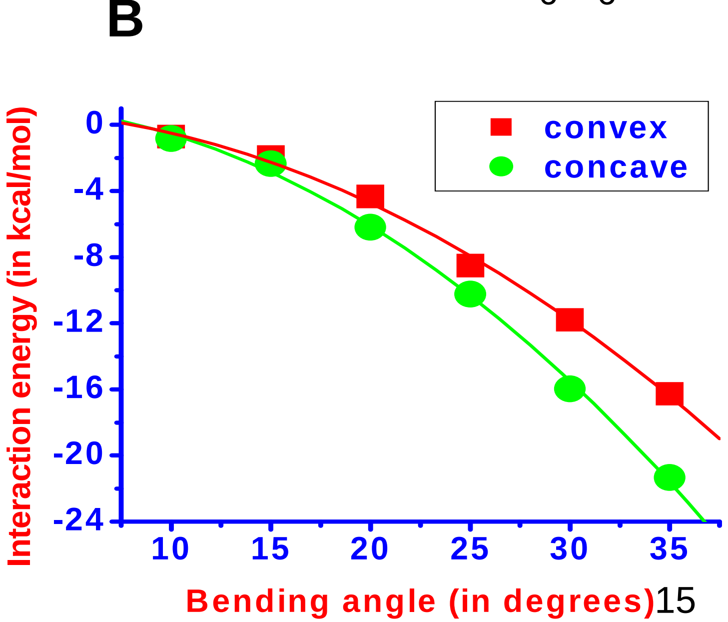


Curvature induced molecular interaction

Electron charge density distribution in Na-C_6H_6 with the bending angle (A) 10° and (B) 35°



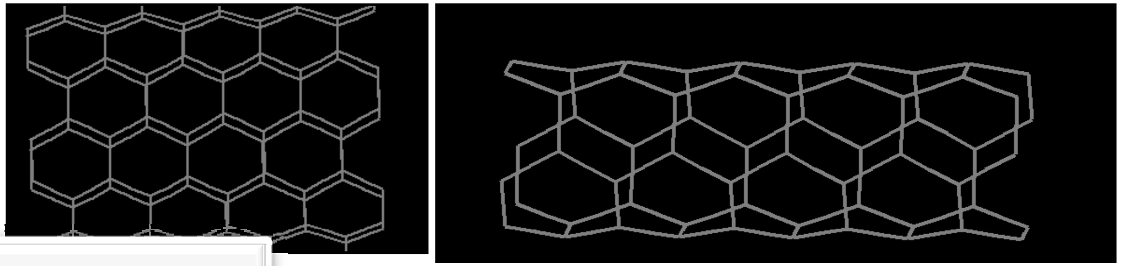




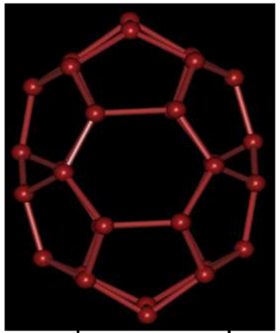
What is the optimum curvature to have the desired property of a nanomaterial ?

- **Chemical reactivity of different carbon nanomaterials**
  - Curvature of the materials
  - Charge at the Surface
  - Aromaticity
    - Role in enhancement of Hydrogen adsorption
      - Molecular Organization

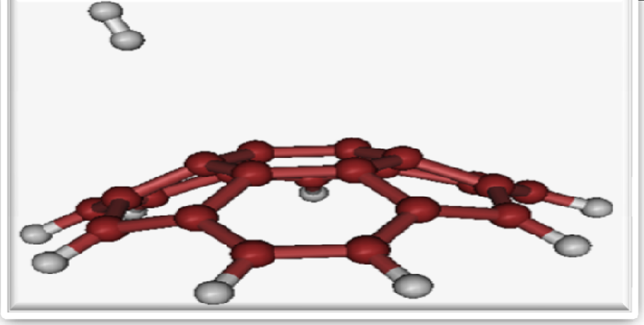
Nanotubes



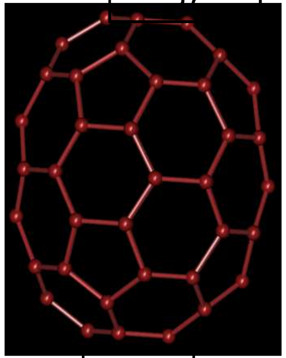
Fullerenes



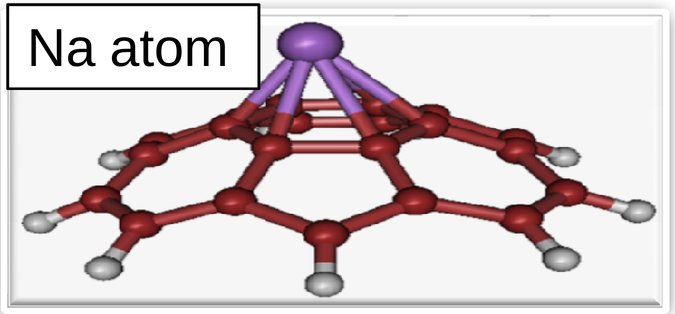
C_{32}



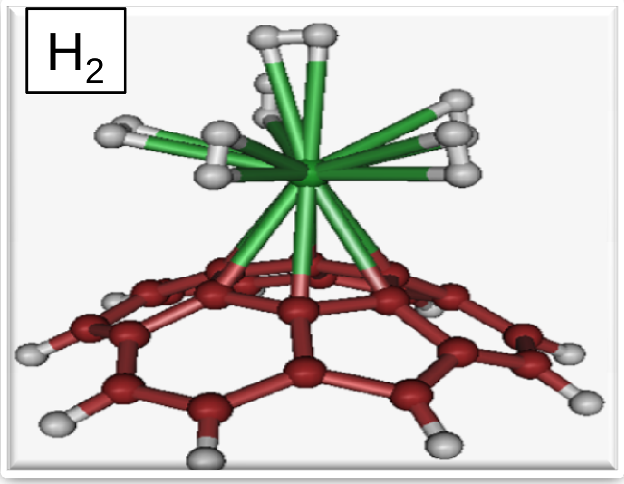
Intra- & inter-curvature in rings



C_{70}



Na atom



H_2

- “Soft matter is the stuff that lies on the borderline between liquid and solid, the stuff that makes the difference between a skeleton and a human being.”

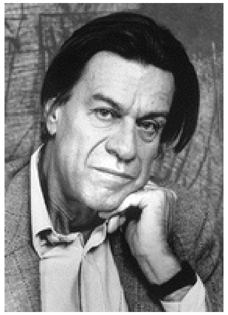
- “Soft matter can be transformed by weak external actions, much as a sculptor deforms the shape of clay by the gentle pressure of a thumb.”

“This is the central and fundamental definition of soft matter.”

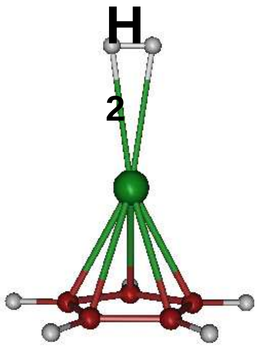
- “The word “Soft” has a double meaning. The materials that one is studying lack the rigid structure of crystalline solids, and the analytical tools that one is using lack the mathematical precision of solid state theory.”

- “Soft matter leaves room for unexpected behaviour, and soft analysis leaves room for imaginative ideas.”

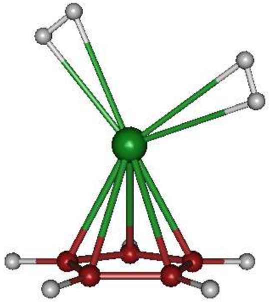
“Fragile Objects, Soft Matter, Hard Science, and the Thrill of Discovery”,
by P.G. de Gennes & J. Badoz (Springer-Verlag, 1996)



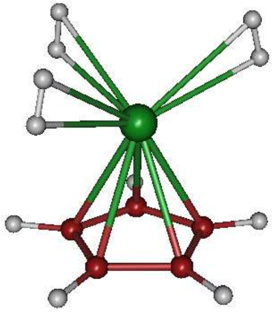
Systematic study of hydrogen interaction with C_5H_5-Na



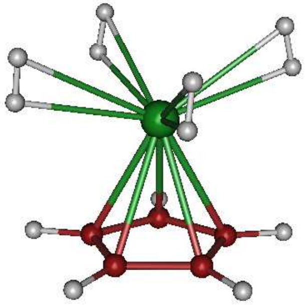
C_5H_5—Na(H_2)



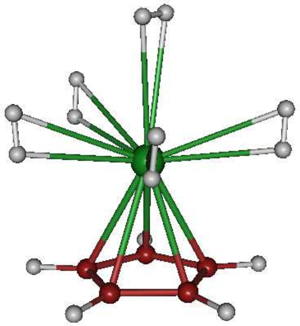
C_5H_5—Na$(H_2)_2$



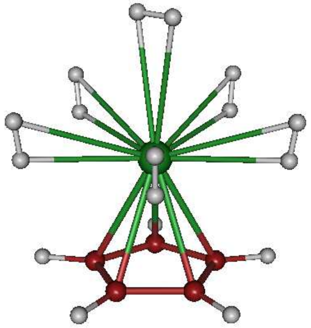
C_5H_5—Na$(H_2)_3$



C_5H_5—Na$(H_2)_4$



C_5H_5—Na$(H_2)_5$



C_5H_5—Na$(H_2)_6$

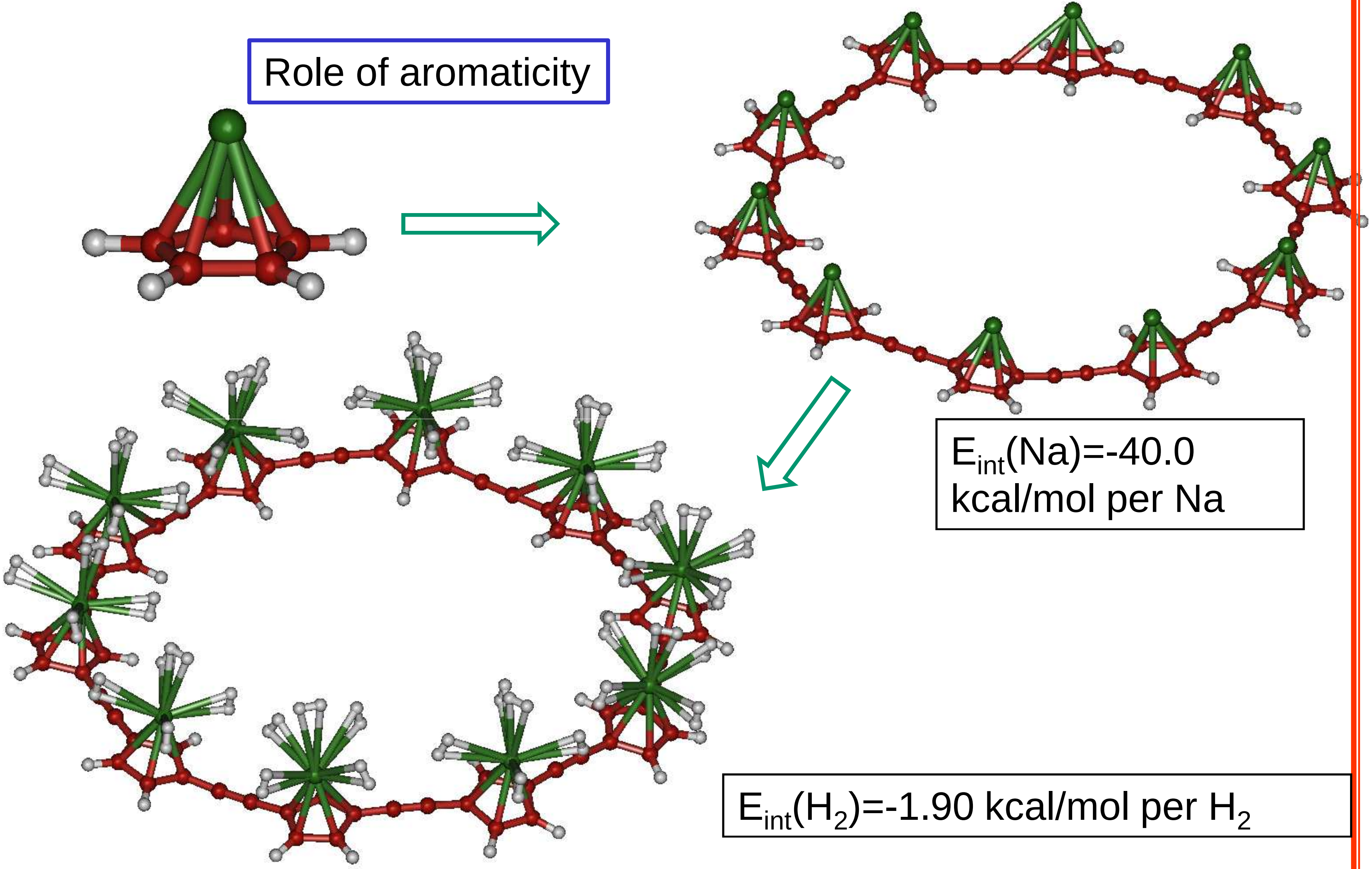
	Q_{Na}		I.E(Kcal)	
	MP2	HLYP	MP2	HLYP
C_5H_5-Na1H_2	0.55	0.55	-2.13	-1.98
C_5H_5-Na2H_2	0.50	0.50	-4.03	-3.84
C_5H_5-Na3H_2	0.45	0.42	-6.16	-5.48
C_5H_5-Na4H_2	0.42	0.41	-8.18	-7.15
C_5H_5-Na5H_2	0.41	0.46	-9.52	-8.36
C_5H_5-Na6H_2	0.34	0.42	-11.54	-9.70

	Q		I.E	
	HLYP	MP2	HLYP	MP2
C_8H_8-Na	0.59	0.63	-34.95	-51.84
C_8H_8-Na1H_2	0.54	0.60	-2.52	-2.88
C_8H_8-Na2H_2	0.44	0.50	-4.60	-5.78
C_8H_8-Na3H_2	0.46	0.53	-6.52	-8.31
C_8H_8-Na4H_2	0.38	0.46	-7.79	-10.35

AROMATICITY is the Key

Molecules to Materials

Role of aromaticity



$E_{int}(Na)$=-40.0 kcal/mol per Na

$E_{int}(H_2)$=-1.90 kcal/mol per H_2

The Journal of Physical Chemistry Letters

LETTER

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Beyond the Gold–Hydrogen Analogy: Doping Gold Cluster with H-atom–O_2 Activation and Reduction of the Reaction Barrier for CO Oxidation

Naresh K. Jena,[†,‡] K. R. S. Chandrakumar,[†] and Swapan K. Ghosh[*,†,‡]

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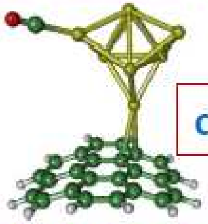
Effect of surface curvature & Effect of H doping on CO adsorption

Au_8

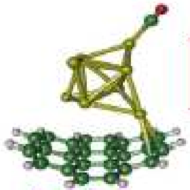
planar

E_{CO} -3.33 k cal /mole



convex

E_{CO} -6.45 k cal /mole



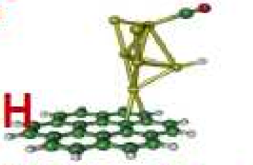
concave

E_{CO} -3.11 k cal /mole

Planar Graphene or curved Carbon Nanotubes are ideal supports apart from oxides

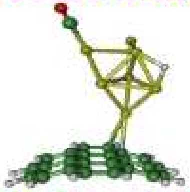
For pristine cluster Au8 –effect of surface curvature-planar, concave or convex plays an important role in deciding the binding of CO

For H-doped gold cluster, doping solely decides the binding energy of CO to the clusters which remains nearly the same for all 3 surfaces- nullifying the surface effect

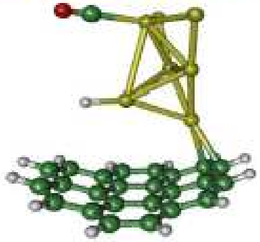


Au_7H

E_{CO} -10.10 k cal /mole



E_{CO} -9.9 k cal /mole



E_{CO} -10.35 k cal /mole

Can CNT play a role in nuclear waste management ?

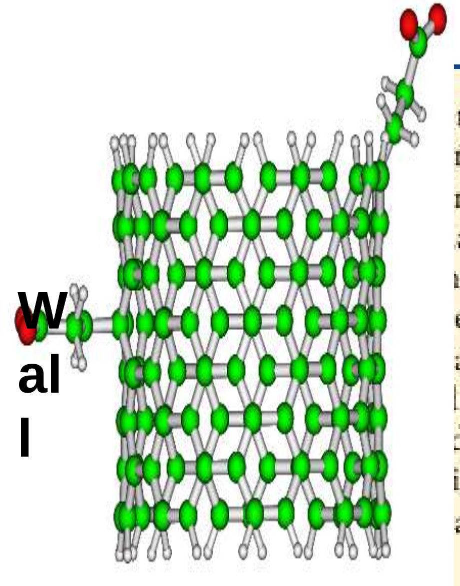
THE JOURNAL OF
PHYSICAL CHEMISTRY A
ARTICLE
pubs.acs.org/JPCA

Designing Novel Materials through Functionalization of Carbon Nanotubes for Application in Nuclear Waste Management: Speciation of Uranyl

CNT - Unique Structure
Solubility Issues-Poor solubility
Functionalization of CNT

Mahesh Sundararajan[†] and Swapan K Ghosh[*,†,‡]

[†]Theoretical Chemistry Section, Bhabha Atomic Research Centre, Mumbai 400 085, India
[‡]Homi Bhabha National Institute, Mumb



ABSTRACT: Understanding the beha … nts in
different environmental conditions is an … rk, we
have investigated the possible interacti … nano-
tubes and uranyl using density functiona … alized
carbon nanotubes can be used to bind … ntly as
compared to their unfunctionalized co … ergies
are sensitive to the nature of the func … arbon
nanotube itself. The binding takes plac … l sites,
although pH could determine the stre … dicted
results correlate well with the recent ex … ies on
carbon nanotubes. These finding are ne … actinide speciation and separation chemistry using carbon
nanotubes.

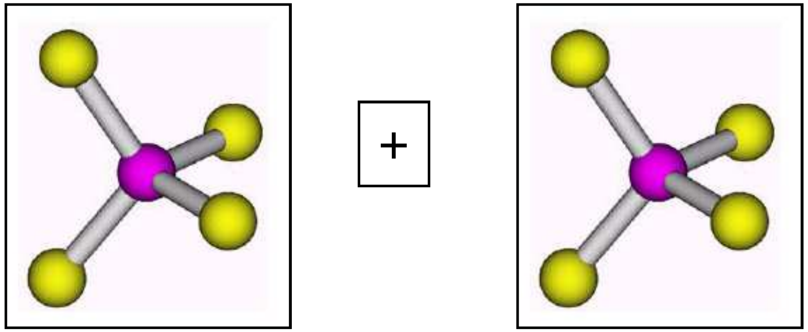
Cluster Assembled Materials

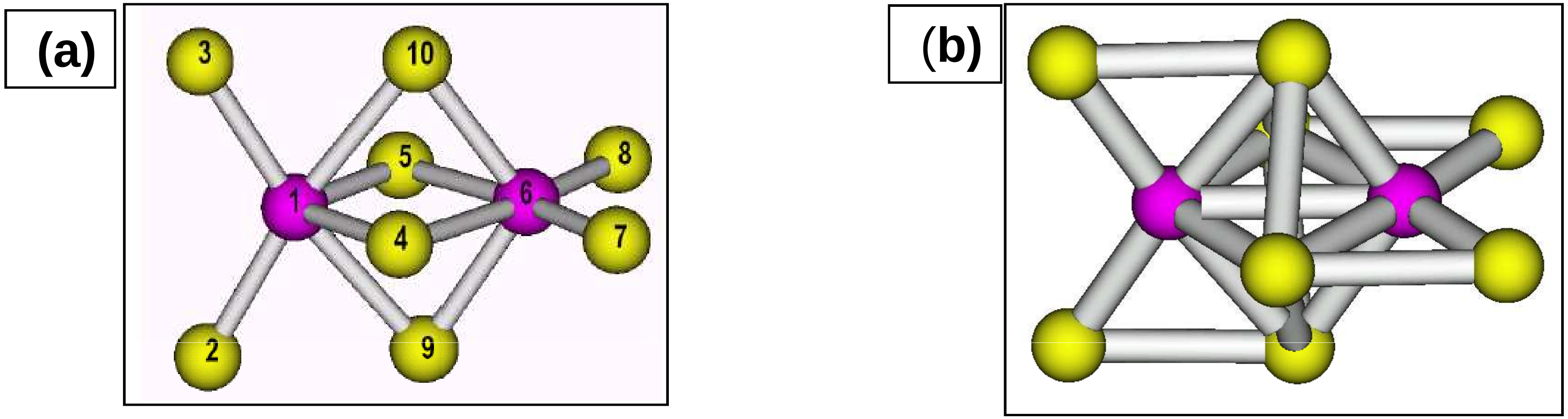
Objective: Design of New/Novel Materials with Desired Properties through Assembly of Clusters (Artificial atoms)

Basic Requirements:

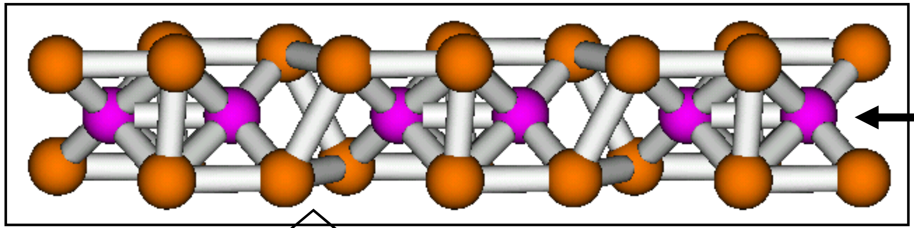
- Building blocks (clusters) must be very stable so that their individual identity is preserved in the new material.
- Intercluster interaction must be very weak to prevent them from collapse for a successful assembly

- Metal/Semiconductor Magic Clusters
- Size-dependent Cluster Properties (Finite Size Effect)
  - Tunable properties

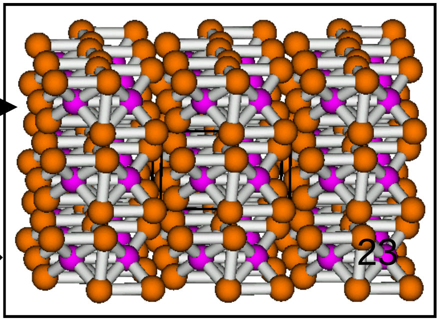




Optimized structures of MAu_4 dimer (M = Ti and Zr) (D_{2d}):
(a) Au-Au bonds are not shown to highlight the M-Au-M bridge bonds (b) both M-Au and Au-Au bonds are shown



proposed



1-D

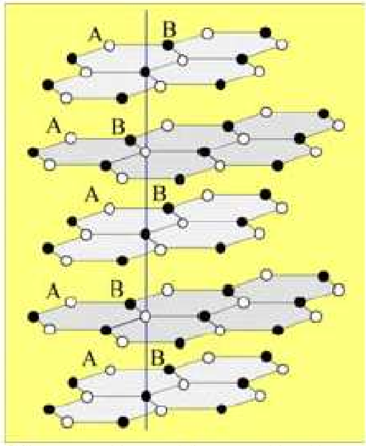
3-D

Molecules → Extended Systems

6-membered Ring as Building block for Graphite, Graphene, Nanotubes

Introduction of Curvature for Nanotubes, Fullerenes & 5-membered Ring for Fullerene

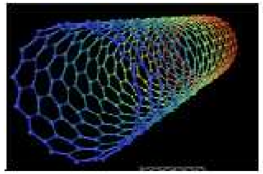
Graphite

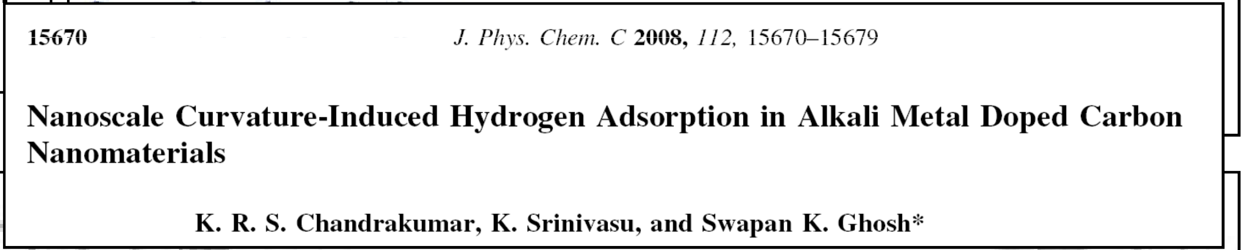


Graphene

Nanotubes

Iijima 1991
Smalley 1993

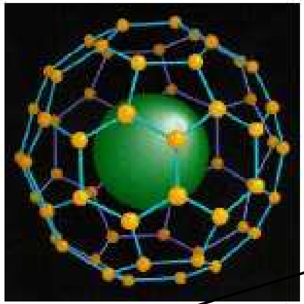




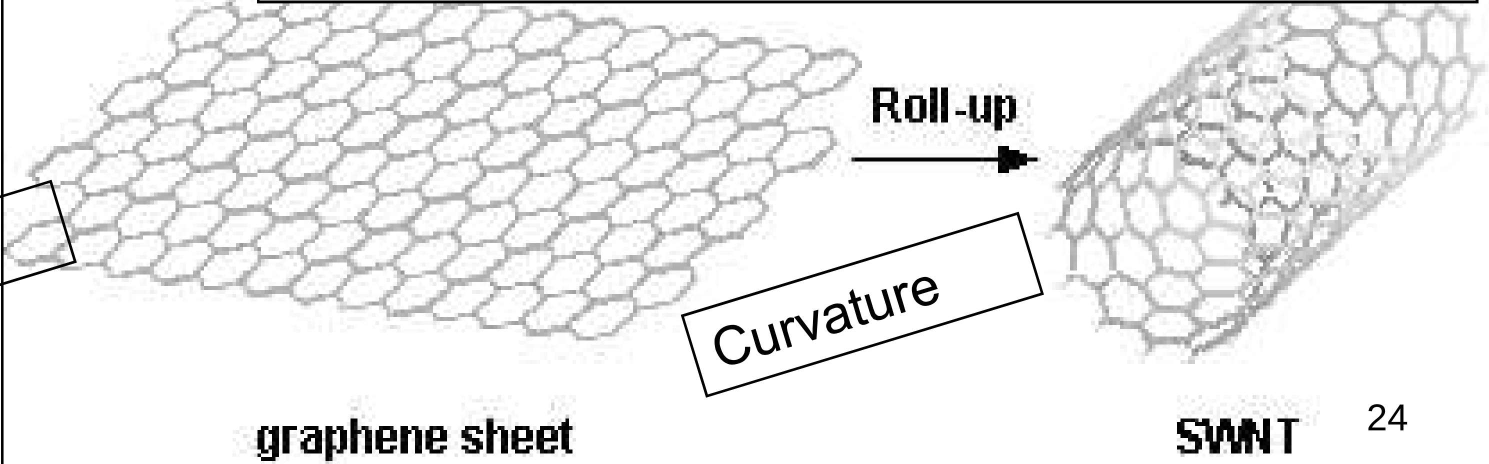
15670 J. Phys. Chem. C **2008,** *112,* 15670–15679

Nanoscale Curvature-Induced Hydrogen Adsorption in Alkali Metal Doped Carbon Nanomaterials

K. R. S. Chandrakumar, K. Srinivasu, and Swapan K. Ghosh*



Confinement



Curvature

Simple Concepts in DFT: Quantum Systems
A LIGHT step to a SOUND interpretation and CURRENT understanding

Highlights: Lattice Model for Molecules

- Atomic Parameters for modelling Molecules
  (Electronegativity, Hardness, Polarizability etc)

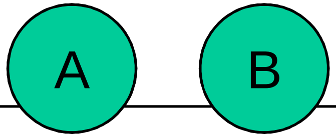
- Molecular electron density $\rho(r)$ as a
  superposition of densities at atomic sites

- Functional Taylor expansion of energy change
  in terms of $\rho(r)$ & re-express in terms of atomic
  charge & dipole, by evaluating moments of density

- Chemical potential equalization to determine these
  quantities, which are now basic variables

Electronegativity (Chemical potential) equalisation Principle

Limitations: *no rigorous quantum mechanical definition*
no theoretical basis for equalisation
no description of covalent binding



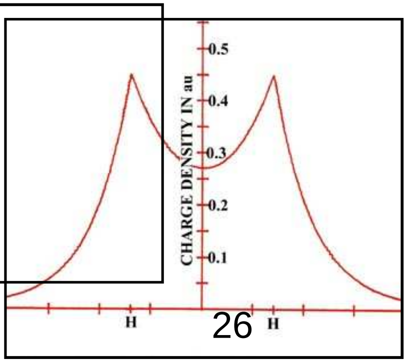
$E[\rho] = \int dr\, v(r)\, \rho(r) + F[\rho]; \quad \mu = \delta E/\delta\rho(r) = v(r) + \delta F[\rho]/\delta\rho(r)$

(Electronegativity) $\chi=-(\partial E/\partial N)=-\int (\delta E/\delta\rho(r))\, (\partial\rho(r)/\partial N)dr$
$= -\mu$ (Chemical potential)

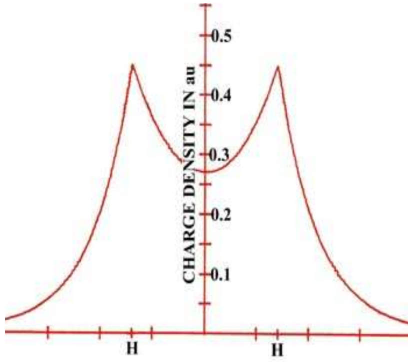
(Hardness) $\chi=(1/2)(\partial^2 E/\partial^2 N)$

$\mu_A=\mu_{0A}+2\eta_A\Delta N_A + 2\eta_{AB}\,\Delta N_B$, for A and B ;
Charge conservation $\Delta N_A + \Delta N_B =0$, $Q = (\mu_{0A} - \mu_{0B})/2\,(\eta_A + \eta_B -\eta_{AB})$
$\Delta E =(1/2)(\mu_{0A} - \mu_{0B})^2/(\eta_A + \eta_B -\eta_{AB})$

Covalent binding: Quantum mechanical effect
no inter-atomic charge transfer
electron delocalisation
inter-atomic spin transfer



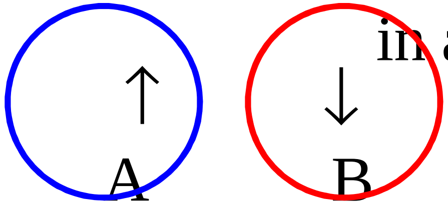
Electronegativity & chemical binding



(1) Electron delocalisation:

charge transfer to the bond region

(2) Spin transfer: Role of unpaired electrons in atoms for covalent bond formation

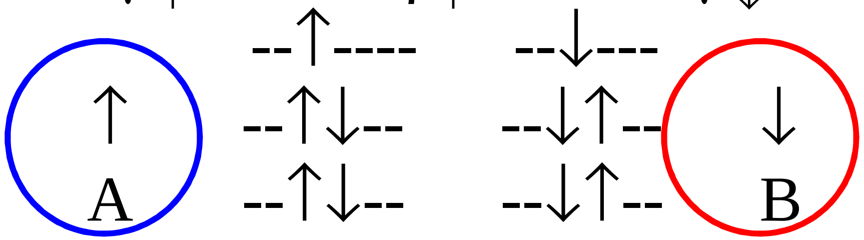


charge density: $\rho(r) = \rho_{\uparrow}(r) + \rho_{\downarrow}(r)$

spin density: $s(r) = \rho_{\uparrow}(r) - \rho_{\downarrow}(r)$

Spin-dependent generalised electronegativity:

$\mu_{\uparrow} = \delta E/\delta\rho_{\uparrow}$ $\qquad$ $\mu_{\downarrow} = \delta E/\delta\rho_{\downarrow}$



Hardness: $\eta_{\uparrow} = (\partial^2 E/\partial N_{\uparrow}^2)$

$\eta_{\downarrow} = (\partial^2 E/\partial N_{\downarrow}^2)$

$\eta_{\uparrow\downarrow} = (\partial^2 E/\partial N_{\uparrow}\,\partial N_{\downarrow})$

- Equalisation of $\mu_{\uparrow}$ and $\mu_{\downarrow}$ in the two atoms determine $\Delta N_{\uparrow}$ and $\Delta N_{\downarrow}$ and hence charge and spin transfer providing measures of ionicity & Covalency.
- Spin transfer accounts for homonuclear binding.
- Charge transfer into the bond region is another contributor.

J. Amer. Chem. Soc.116, 3943 (1994); J. Chem. Sci. 117, 401 (2005); JMS THEOCHEM 943, 178(2010)

For a polyatomic molecule $Ab_{n\ ,}$ the energy change

$$\begin{aligned}\Delta E = {} & \mu_\alpha^{\mathrm{A}} \Delta N_\alpha^{\mathrm{A}} + \mu_\beta^{\mathrm{A}} \Delta N_\beta^{\mathrm{A}} + n\mu_\alpha^{\mathrm{B}} \Delta N_\alpha^{\mathrm{B}} + n\mu_\beta^{\mathrm{B}} \Delta N_\beta^{\mathrm{B}} + \\ & \eta_\alpha^{\mathrm{A}}(\Delta N_\alpha^{\mathrm{A}})^2 + \eta_\beta^{\mathrm{A}}(\Delta N_\beta^{\mathrm{A}})^2 + n\eta_\alpha^{\mathrm{B}}(\Delta N_\alpha^{\mathrm{B}})^2 + n\eta_\beta^{\mathrm{B}}(\Delta N_\beta^{\mathrm{B}})^2 + \\ & \eta_{\alpha\beta}^{\mathrm{A}}(\Delta N_\alpha^{\mathrm{A}})(\Delta N_\beta^{\mathrm{A}}) + n\eta_{\alpha\beta}^{\mathrm{B}}(\Delta N_\alpha^{\mathrm{B}})(\Delta N_\beta^{\mathrm{B}}) + \\ & n\eta_{\alpha\alpha}^{\mathrm{A,B}}(\Delta N_\alpha^{\mathrm{A}})(\Delta N_\beta^{\mathrm{B}}) + n\eta_{\beta\beta}^{\mathrm{A,B}}(\Delta N_\beta^{\mathrm{A}})(\Delta N_\beta^{\mathrm{B}}) + \\ & n\eta_{\alpha\beta}^{\mathrm{A,B}}(\Delta N_\alpha^{\mathrm{A}})(\Delta N_\beta^{\mathrm{B}}) + n\eta_{\beta\alpha}^{\mathrm{A,B}}(\Delta N_\beta^{\mathrm{A}})(\Delta N_\alpha^{\mathrm{B}})\end{aligned}$$

For a diatomic molecule AB

$$\Delta E_{\mathrm{AA}}^{\mathrm{I}} = (\mu_\alpha^{\mathrm{A}} - \mu_\beta^{\mathrm{A}})\Delta N_\alpha^{\mathrm{A}}$$

$$\Delta N_\alpha^{\mathrm{A}} = -\Delta N_\beta^{\mathrm{A}} = -(\mu_\alpha^{\mathrm{A}} - \mu_\beta^{\mathrm{A}})/(2\eta_\alpha^{\mathrm{A}} + 2\eta_\beta^{\mathrm{A}} - 2\eta_{\alpha\beta}^{\mathrm{A}})$$

For general polyatomic molecules,Linear equations for the atomic charges & dipoles

$$\sum_{\beta=1}^{N} b_{\alpha\beta}^{0,0}\delta q_\beta + \sum_{\beta=1}^{N} \vec{c}_{\alpha\beta}^{\,0,1}\cdot\delta\mathbf{p}_\beta = d_\alpha,\ \alpha=1,\ 2,\ ...,\ N,$$

$$\sum_{\beta=1}^{N} \vec{h}_{\alpha\beta}^{1,0}\delta q_\beta + \sum_{\beta=1}^{N} \overleftrightarrow{k}_{\alpha\beta}^{1,1}\cdot\delta\mathbf{p}_\beta = \vec{s}_\alpha,\quad \alpha,=1, 2, \ldots, N,$$

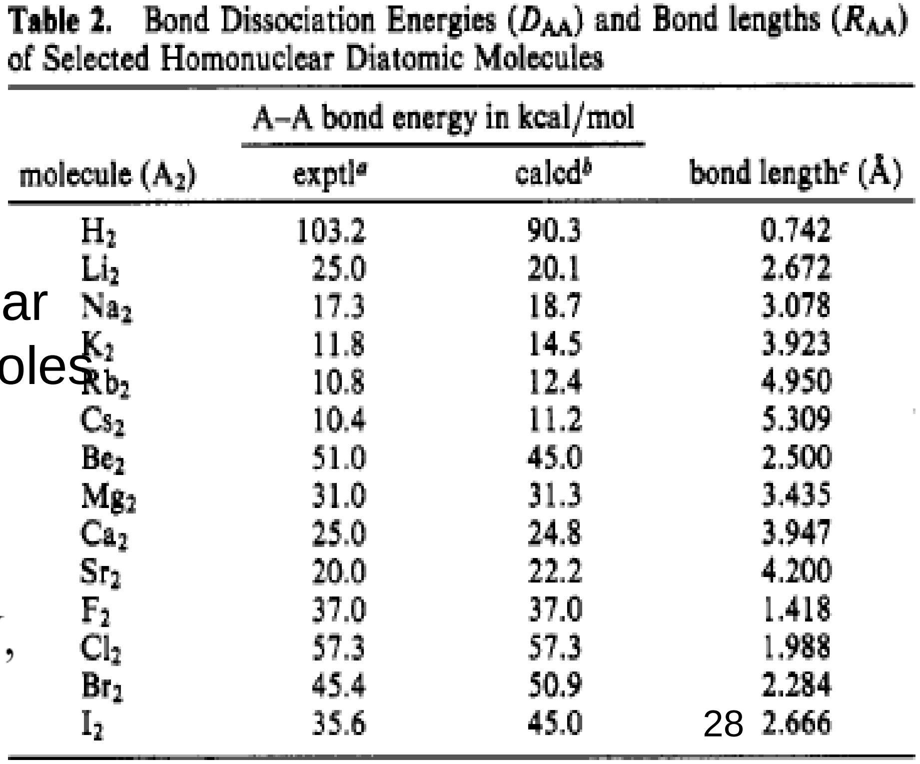
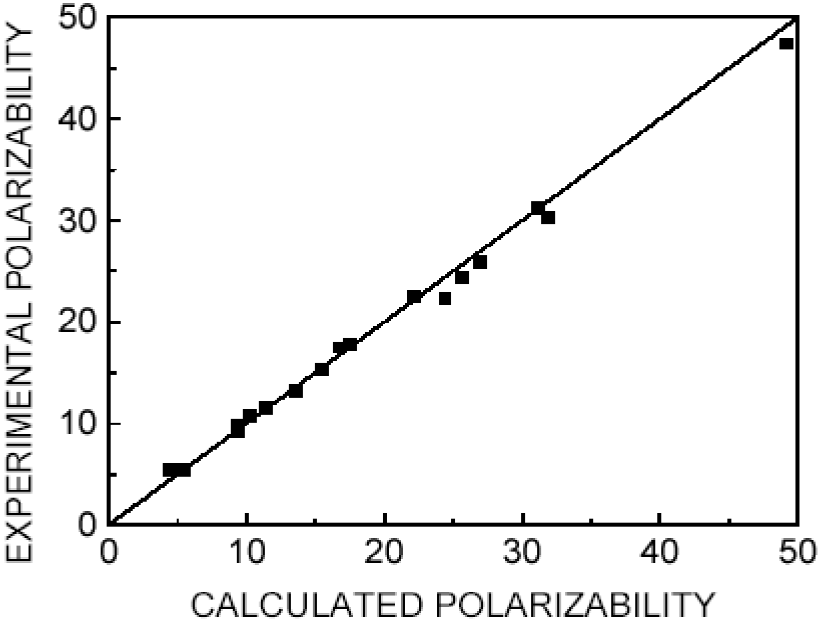


Table 2. Bond Dissociation Energies (D_{AA}) and Bond lengths (R_{AA}) of Selected Homonuclear Diatomic Molecules

molecule (A_2)	A–A bond energy in kcal/mol exptl[a]	 calcd[b]	bond length[c] (Å)
H_2	103.2	90.3	0.742
Li_2	25.0	20.1	2.672
Na_2	17.3	18.7	3.078
K_2	11.8	14.5	3.923
Rb_2	10.8	12.4	4.950
Cs_2	10.4	11.2	5.309
Be_2	51.0	45.0	2.500
Mg_2	31.0	31.3	3.435
Ca_2	25.0	24.8	3.947
Sr_2	20.0	22.2	4.200
F_2	37.0	37.0	1.418
Cl_2	57.3	57.3	1.988
Br_2	45.4	50.9	2.284
I_2	35.6	45.0	2.666

Charges for CH_4 molecule

Atom	Charge model DFT	Charge DFT
C	-0.484	-0.497
H	0.121	0.124
H	0.121	0.124
H	0.121	0.124
H	0.121	0.124



Charges for C_2H_6 molecule

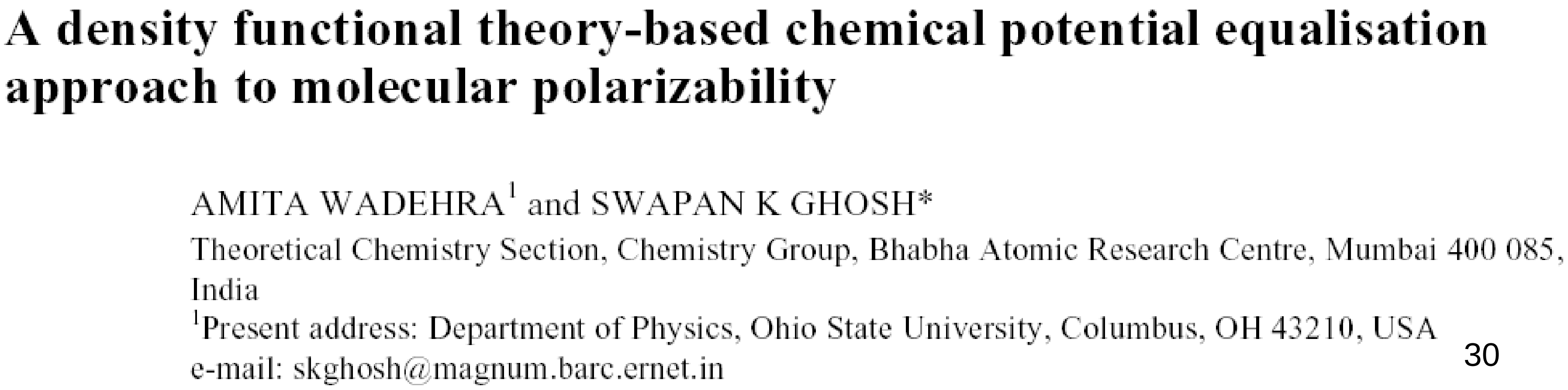
Atom	Charge model DFT	Charge DFT
C	-0.339	-0.356
H	0.113	0.119
H	0.113	0.124
C	-0.339	-0.360
H	0.113	0.119
H	0.113	0.119
H	0.113	0.119
H	0.113	0.119

An Atomic Lattice Model for Molecules

Coarse graining of electron density in terms
of partial atomic charges & atomic dipoles

- *Modelling chemical binding and response properties in terms of atomic charges & dipoles, the zeroeth and first moments of the electron density rather than the full function*
- *Binding energy through a functional perturbation in terms of the electron density change*
- *Density Functional Perturbation Theory*

J. Chem. Sci., Vol. 117, No. 5, September 2005, pp. 401–409. © Indian Academy of Sciences.



A density functional theory-based chemical potential equalisation approach to molecular polarizability

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Response of molecular assemblies to an external electric field

$$E_v[\rho(\mathbf{r})] = \int d\mathbf{r}\rho(\mathbf{r})v(\mathbf{r}) + F[\rho(\mathbf{r})]$$

$$\mu = \frac{\delta E_v[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} = v(\mathbf{r}) + \frac{\delta F[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} \qquad \eta(\mathbf{r},\mathbf{r}') = \left(\frac{\delta^2 F[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right)$$

Binding energy through a functional perturbation in terms of the electron density change

$$\Delta E = E[\rho(\mathbf{r}) + \delta\rho(\mathbf{r}), v(\mathbf{r}) + \delta v(\mathbf{r})] - E[\rho(\mathbf{r}), v(\mathbf{r})]$$

$$= \int d\mathbf{r}\left(\frac{\delta E[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})}\right)_{v(\mathbf{r})} \delta\rho(\mathbf{r}) + \int d\mathbf{r}\left(\frac{\delta E[\rho(\mathbf{r})]}{\delta v(r)}\right)_{\rho(\mathbf{r})} \delta v(\mathbf{r})$$

$$+ \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}'\left(\frac{\delta^2 E[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right)_{v(\mathbf{r})} \delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')$$

$$+ \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}'\left(\frac{\delta^2 E[\rho(\mathbf{r})]}{\delta v(\mathbf{r})\delta v(\mathbf{r}')}\right)_{\rho(\mathbf{r})} \delta v(\mathbf{r})\delta v(\mathbf{r}')$$

$$+ \iint d\mathbf{r}d\mathbf{r}'\left(\frac{\delta^2 E[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})\delta v(\mathbf{r}')}\right)\delta\rho(\mathbf{r})\delta v(\mathbf{r}').$$

Model the molecular density in terms of atomic ones

$$\delta\rho(\mathbf{r}) = \sum_{\alpha} \delta\rho_{\alpha}(\mathbf{r}) = \sum_{\alpha} \delta\rho_{\alpha}(\mathbf{r}_{\alpha}),$$

where $\mathbf{r}_{\alpha} = \mathbf{r} - \mathbf{R}_{\alpha}$ denotes the atom-centered coordinate with the origin located at the α-th atom.

$$\mu_{\alpha} = \mu_{\alpha}^{0} + \delta v(\mathbf{r}_{\alpha}) + \int d\mathbf{r}' \eta(\mathbf{r}_{\alpha}, \mathbf{r}')\delta\rho(\mathbf{r}')$$

Express the chemical potential in terms of density moments

$$q_{\beta} = -\Delta N_{\beta}^{el} = -\int \mathrm{d}\mathbf{r}'_{\beta}\delta\rho_{\beta}(\mathbf{r}'_{\beta}) \qquad \mathbf{p}_{\beta} = \int \mathrm{d}\,{}'_{\beta}\mathbf{r}'\,\delta\rho_{\beta}(\mathbf{r}_{,}\,)$$

to obtain

$$\mu_{\alpha} = \mu_{\alpha}^{0} + \delta v(\alpha) - \sum_{\beta} \eta(\alpha, \beta) q_{\beta} + \sum_{\beta} \nabla_{\beta} \eta(\alpha, \beta)\, \mathbf{p}_{\beta}$$

$$0 = \mathbf{E}_{\alpha} + \sum_{\beta} \nabla_{\alpha} \eta(\alpha, \beta) q_{\beta} - \sum_{\beta} \nabla_{\alpha} \nabla_{\beta} \eta(\alpha, \beta) \mathbf{p}_{\beta}$$

$$\mu_\alpha = \mu_\alpha^0 - \eta_\alpha^0 q_\alpha + \left(\phi_\alpha^0 - \sum_{\beta=1}^{N}{}' \, \eta_{\alpha\beta}^{0,0} q_\beta + \sum_{\beta=1}^{N}{}' \, \vec{\eta}_{\alpha\beta}^{\,0,1} \cdot \mathbf{p}_\beta \right)$$

$$\alpha = 1,\ 2,\ \ldots,\ N$$

$$\delta \mathbf{p}_\alpha = \overset{\leftrightarrow}{\alpha}_\alpha \cdot \left(\mathbf{E}^0 - \sum_{\beta=1}^{N}{}' \, \overset{\leftrightarrow}{\eta}_{\alpha\beta}^{1,1} \delta q_\beta - \sum_{\beta=1}^{N}{}' \, \overset{\leftrightarrow}{\eta}_{\alpha\beta}^{1,1} \delta \mathbf{p}_\beta \right)$$

$$\alpha = 1, 2, \ldots, N,$$

Linear equations for the atomic charges & dipoles

$$\sum_{\beta=1}^{N} b_{\alpha\beta}^{0,0} \delta q_\beta + \sum_{\beta=1}^{N} \vec{c}_{\alpha\beta}^{\,0,1} \cdot \delta \mathbf{p}_\beta = d_\alpha ,\ \ \alpha = 1,\ 2,\ \ldots,\ N,$$

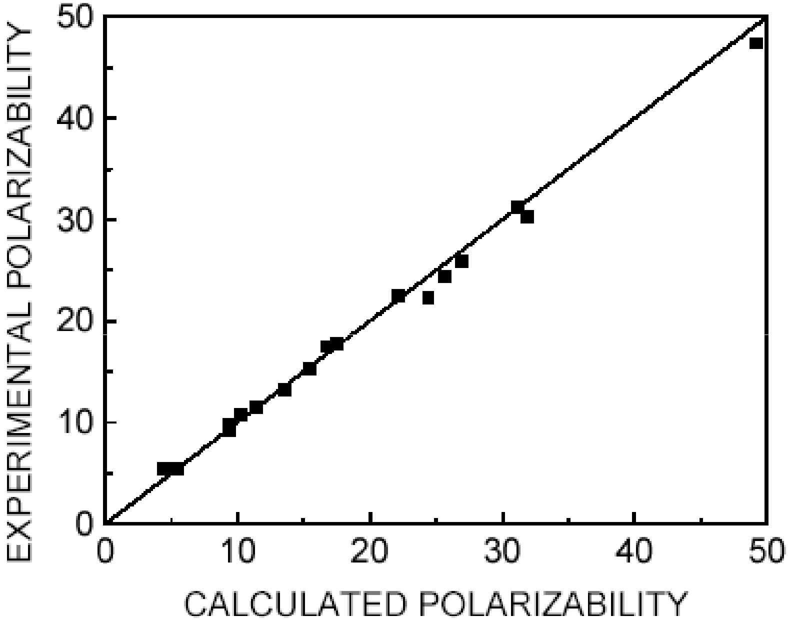
$$\sum_{\beta=1}^{N} \vec{h}_{\alpha\beta}^{1,0} \delta q_\beta + \sum_{\beta=1}^{N} \overset{\leftrightarrow}{k}_{\alpha\beta}^{1,1} \cdot \delta \mathbf{p}_\beta = \vec{s}_\alpha , \quad \alpha, = 1, 2, \ldots, N,$$

Dipole moment & hence the polarizability from atomic charges & dipoles

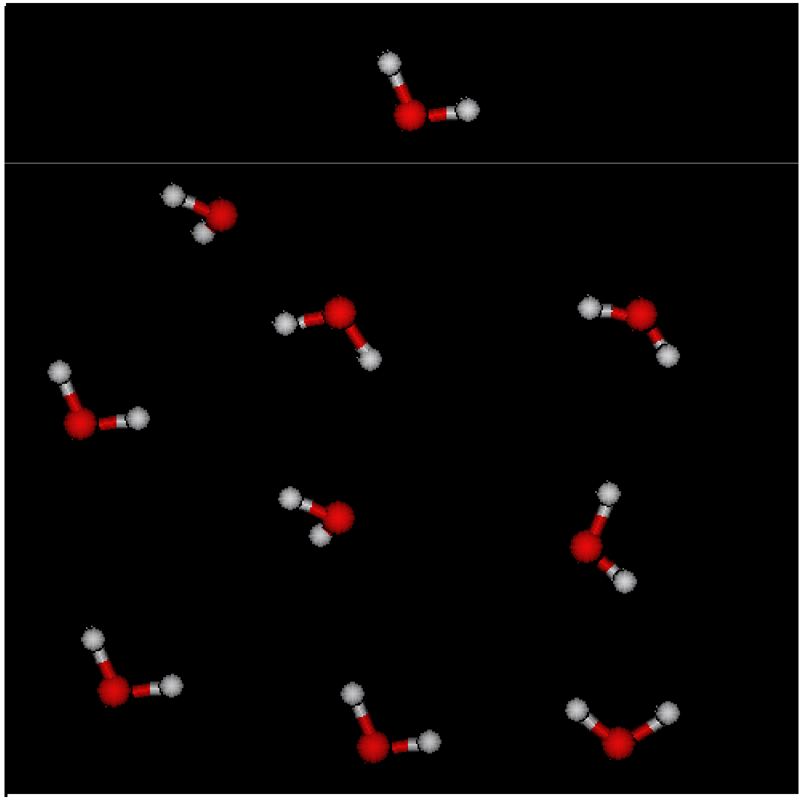
$$\delta \mathbf{p}_{mol} = \sum_{\alpha=1}^{N} (\mathbf{R}_\alpha \delta q_\alpha + \delta \mathbf{p}_\alpha)$$

Table 2. Polarizability α (in a.u.) of simple molecular systems.

Molecule	Calculated α	Experimental α
HCl	17·11(a)	17·76
	17·12(b)	
CO	12·92	13·17
	13·21	
H_2O	9·72	9·79
	8·54	
CO_2	16·65	19·66
	17·42	
C_2H_2	21·99	22·49
	22·25	
HCHO	15·02	18·92
	15·20	
CH_4	20·70	17·52
	20·82	
CCl_4	79·03	70·93
	79·29	
CH_3Cl	34·38	31·2
	34·51	
$CHCl_3$	63·56	64·17
	63·77	



- Calculation of binding energy & polarizability of molecules and molecular assemblies in terms of atomic ones
- A self consistent calculation of intermolecular interaction Potential
- Useful in Simulation: Polarizable point charge-point dipole model for water



- Car-Parrinello type simulation
using atomic charge and atomic dipole variables
rather than the full electron density.
- The effective Lagrangian is
constructed using these variables.

Car Parrinello type ab-initio simulation using atomic charge & dipoles as dynamical variables

Effective Lagrangian:

$$L = \Sigma_i^{mol} \Sigma_\alpha^{atom} \left[(1/2) m_\alpha \dot{\mathbf{R}}_{i\alpha}{}^2 + (1/2) m_q q_{i\alpha}{}^2 + (1/2) m_p \mathbf{p}_{i\alpha}{}^2 \right] - U(\{ q_{i\alpha} \}, \{ \mathbf{p}_{i\alpha} \}, \{ \mathbf{R}_{i\alpha} \}) - \lambda \Sigma_i \Sigma_\alpha q_{i\alpha} + \text{(geometry constraints)}$$

Action principle:

$$m_\alpha \ddot{\mathbf{R}}_{i\alpha} = - (\partial U / \partial \mathbf{R}_{i\alpha}) + \text{(geometry constraints terms)}$$

$$m_q \cdot q_{i\alpha} = - (\partial U / \partial q_{i\alpha}) - \lambda$$

$$m_p \mathbf{p}_{i\alpha} = - (\partial U / \partial \mathbf{p}_{i\alpha})$$

Car Parrinello type ab-initio simulation using atomic charge & dipoles as dynamical variables

Effective Lagrangian:

$$L= \Sigma_i^{mol}\Sigma_\alpha^{atom}\ [(1/2)m_\alpha\, \dot{\mathbf{R}}_{i\alpha}{}^2 +($$

$$+(1/2)m_p\, \dot{\mathbf{p}}_{i\alpha}{}^2\ ]$$

$$- U(\{ q_{i\alpha} \},\{\mathbf{p}_{i\alpha} \},\{\mathbf{R}_{i\alpha} \})$$

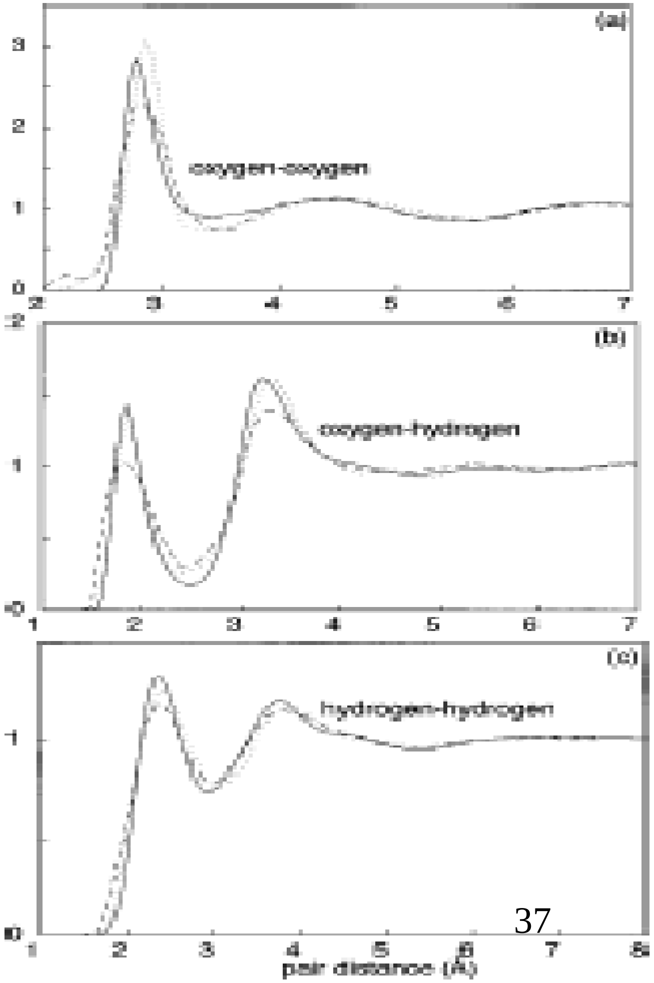
$$- \lambda\ \Sigma_i\Sigma_\alpha\ q_{i\alpha} + (\text{geometry}$$

Action principle:

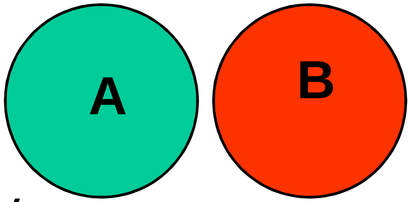
$$m_\alpha\, \ddot{\mathbf{R}}_{i\alpha} = - (\partial U/\partial \mathbf{R}_{i\alpha}) + (\text{geomet}$$

$$m_q\, \ddot{q}_{i\alpha} = - (\partial U/\partial q_{i\alpha}) - \lambda$$

$$m_p\, \ddot{\mathbf{p}}_{i\alpha} = - (\partial U/\partial \mathbf{p}_{i\alpha})$$



Miedema theory & heat of formation of alloys



Heat of formation of AB alloy

$$\Delta H_{AB} = -P(\chi_A - \chi_B)^2 + Q\,[(\rho_{ws}{}^{A})^{1/3} - (\rho_{ws}{}^{B})^{1/3}]^2$$

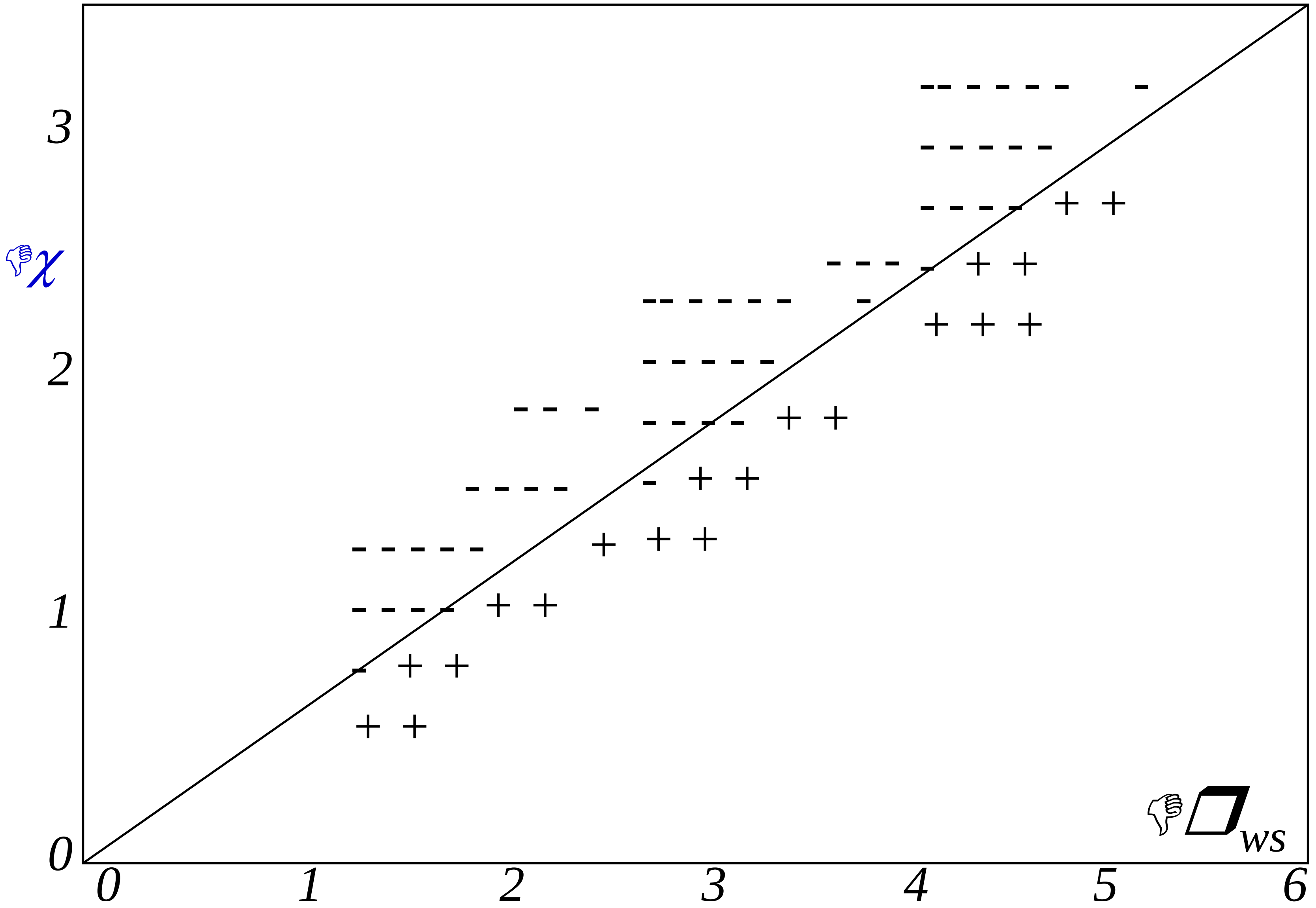
$\chi \rightarrow$ electronegativity ; $\rho_{ws} \rightarrow$density at the boundary

Volume change on alloy formation (chemical origin)

$$\Delta V \approx P(\chi_A - \chi_B) + \frac{[(\rho_{ws}{}^{A})^{-1} - (\rho_{ws}{}^{B})^{-1}]}{[(\rho_{ws}{}^{A})^{-1/3} - (\rho_{ws}{}^{B})^{-1/3}]^{-1}}$$

Solid solubilities

Linear relation between metal compressibility and electron density at the boundary



Sign of heat of formation for alloys of two transition metals plotted as a function of the difference of electronegativity, 🖓χ and the discontinuity of electron density, 🖓❒$_{ws}$

From CLUSTERS
to
CLUSTER ASSEMBLIES

Carbon clusters:

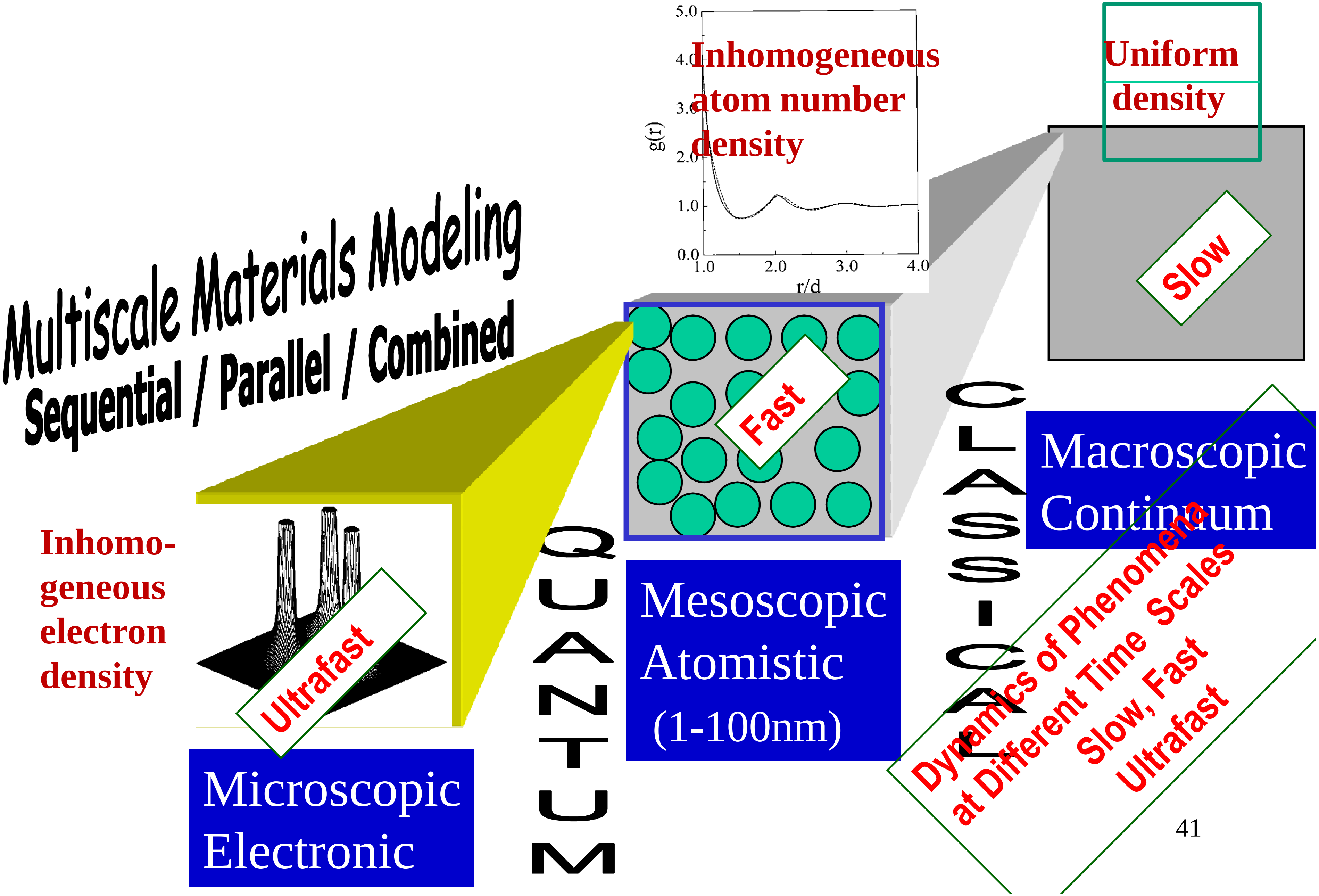
Decorated as Functional Materials

Metal clusters:

Forming assemblies leading to
Functional Materials

Cluster Assembled Materials

Concept of Density at Different Length Scales:



Multiscale Materials Modeling

Sequential / Parallel / Combined

Inhomogeneous atom number density

Uniform density

Slow

Fast

Ultrafast

Inhomo-geneous electron density

QUANTUM

CLASSICAL

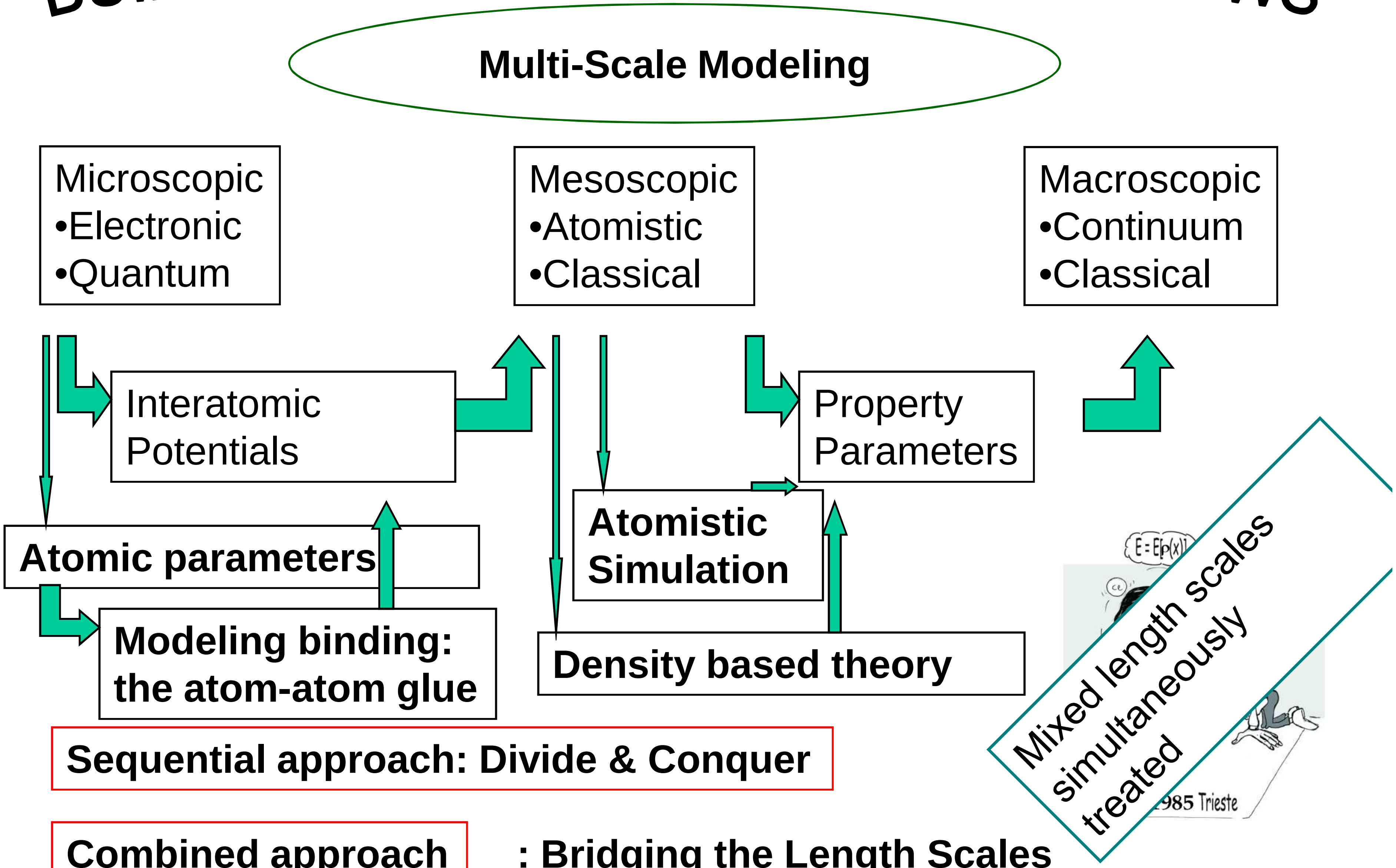
Microscopic Electronic

Mesoscopic Atomistic (1-100nm)

Macroscopic Continuum

Dynamics of Phenomena at Different Time Scales Slow, Fast Ultrafast

BUILDING BRIDGES & OPENING WINDOWS



Multi-Scale Modeling

Microscopic
- Electronic
- Quantum

Mesoscopic
- Atomistic
- Classical

Macroscopic
- Continuum
- Classical

Interatomic Potentials

Property Parameters

Atomistic Simulation

Atomic parameters

Modeling binding: the atom-atom glue

Density based theory

Mixed length scales simultaneously treated

Sequential approach: Divide & Conquer

Combined approach **: Bridging the Length Scales**

: Car-Parrinello & Analogous approaches

Practical Implementation of DFT

Quantum DFT

One-particle Schrodinger eqn.

$\{-(1/2)\nabla^2 + v(r)\}\, \psi_i = \varepsilon_i \psi_i$

Non-interacting particles

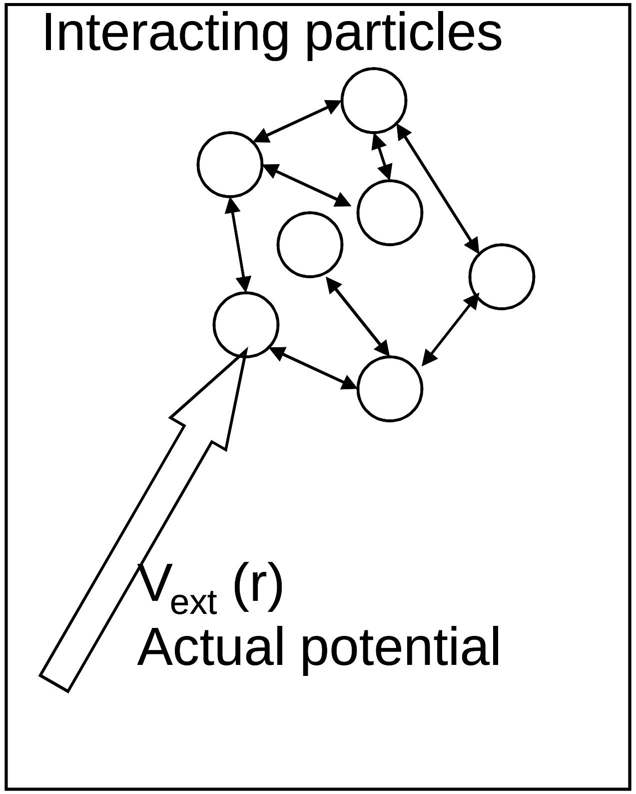
Classical DFT

Boltzmann distribution

$\rho_\alpha(r) = \rho_\alpha^0 \exp(-v_\alpha(r)/kT)$

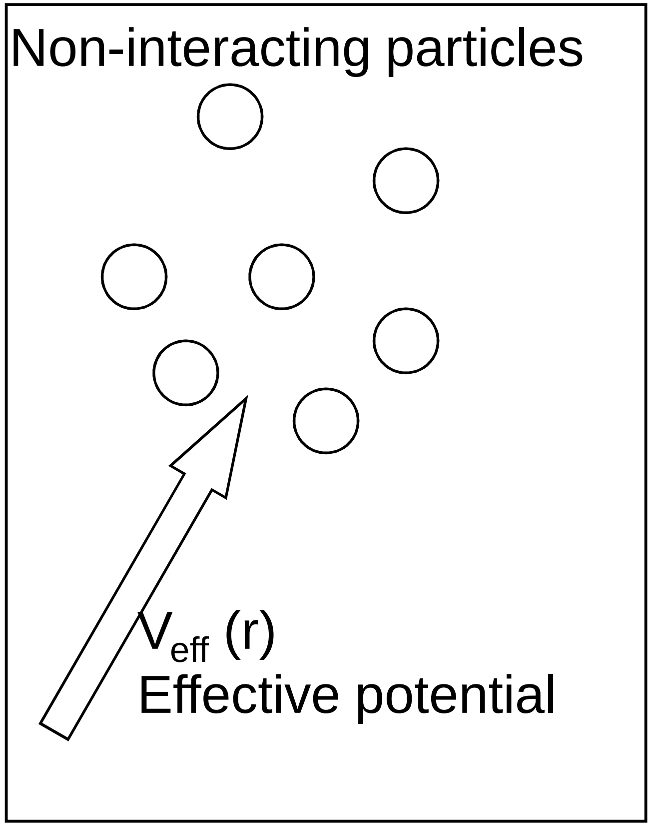
Real interacting system

Concept of noninteracting particles moving in an effective potential



Interacting particles

V_{ext} (r)
Actual potential



Non-interacting particles

V_{eff} (r)
Effective potential

Practical Implementation of DFT

Quantum DFT

One-particle Schrodinger eqn.

$\{-(1/2)\nabla^2 + v(r)\}\,\psi_i = \varepsilon_i \psi_i$

Non-interacting particles

Classical DFT

Boltzmann distribution

$\rho_\alpha(r)=\rho_\alpha^0 \exp(-v_\alpha(r)/kT)$

Real interacting system

Concept of noninteracting particles moving in an effective potential

Kohn-Sham equation: Effective one-particle Schrodinger eqn.

$\boldsymbol{\{-(1/2)\nabla^2 + v_{eff}(r)\}\,\psi_i = \varepsilon_i \psi_i}$

$\rho(r)=\Sigma\, n_i |\psi_i|^2$

Energy $E = \int dr\, v(r)\rho(r) + T_s[\rho(r)] + E_{COUL}[\rho] + E_{xc}[\rho]$

$v_{eff}(r; \rho)= v(r) + (\delta E_{COUL}[\rho]/\delta\rho) + (\delta E_{xc}[\rho]/\delta\rho)$

Kinetic energy functional (exact)

Exchange correlation energy functional (need approximation)

Density equation: Effective Boltzmann like distribution

$\boldsymbol{\rho_\alpha(r)=\rho_\alpha^0 \exp(-v_{eff,\alpha}(r)/kT)}$

Free Energy $F = \int dr\, v(r)\rho(r) + F_{id}[\rho(r)]+ F_{ex}[\rho(r)]$

$v_{eff}(r; \rho)= v(r) + kT\, C^{(1)}(r;\rho)$

where $kT\, C^{(1)}(r;\rho) = (\delta F_{ex}[\rho]/\delta\rho)$

Ideal gas free energy functional: Classical entropy terms (exact)

Excess free energy functional (need approximation)

Density Functional Theory: Basics

The grand potential (ground state energy) of a many-particle system characterized by an external potential v(r) is a unique functional $\Omega[\rho]$ of its single-particle density $\rho(r)$, given by

$$\Omega[\rho] = F[\rho] + \int dr\, \rho(r)\, \{v(r) - \mu\} \qquad (1)$$

and is minimum for the true equilibrium density. Here μ is the chemical potential and $F[\rho]$ is the intrinsic Helmholtz free energy.

How to determine the density $\rho(r)$:
Either (i) Solve the corresponding Euler equation:

$$\{\delta\Omega/\delta\rho(r)\} - \mu = 0 \qquad (2)$$

or, (ii) Use a parametrised density and minimize $\Omega[\rho]$ with respect to the parameters of the density expression.

Obtain the grand potential by using the resulting density into Eq.(1).

Density Functional Theory: Basics

Practical Implementation:

1) Exact expression of the functional F[ρ] is unknown and hence is to approximated.
2) The functional F[ρ] is known for limiting cases, such as system with uniform density ρ_0. This forms the basis of (i) a perturbative approach in terms of $[\rho(r)-\rho_0]$,
   (ii) a weighted density approach where the free energy density or the correlation function is evaluated using a weighted density $\rho_{av}(r) = \int dr' \rho(r') w(r, r')$.

Important Issues:

1) Inhomogeneous density profile can be obtained for a system subjected to an external potential.
2) The theory is however valid in the limit of zero external potential, and hence been immensely successful for the study of appearance of homogeneous or inhomogeneous density, as a consequence of fluctuations.

Density Functional Theory: Basics

1) Quantum Systems : $E_v[\rho] = F[\rho] + \int dr\, \rho(r)\, v(r)$

$F[\rho] = E_{kin}[\rho] + E_{coul}[\rho] + E_{xc}[\rho]$

Approximate $E_{xc}[\rho]$ using LDA or its variants.

2) Classical Systems: $\Omega[\rho] = F[\rho] + \int dr\, \rho(r)\, \{v(r) - \mu\}$

$F[\rho] = E_{ideal}[\rho] + E_{int}[\rho] + F_{ex}[\rho]$

Approximate $F_{ex}[\rho]$ using perturbative or WDA approach.

Solve the corresponding Euler equation:

(1) $\{\delta E_v/\delta\rho(r)\} - \mu = 0$, (2) $\{\delta\Omega/\delta\rho(r)\} - \mu = 0$

or, (ii) Use a parametrised density and minimize $E_v[\rho]$ or $\Omega[\rho]$ with respect to the parameters of the density expression.

QUANTUM MECHANICS of MOLECULES, CLUSTERS, SOLIDS

An Electron Density Description

Hard Matter

$\{-(1/2)\nabla^2 + v_{eff}(r)\}\ \psi_i = \varepsilon_i \psi_I\ ; \quad \rho(r)=\Sigma\ n_i |\psi_i|^2$

$v_{eff}(r;\rho) = v(r) + (\delta E_{COUL}[\rho]/\delta\rho) + (\delta E_{xc}[\rho]/\delta\rho)$

Interparticle correlations

Statistical mechanics of LIQUIDS:
A Mesoscopic Density Description

Soft Matter

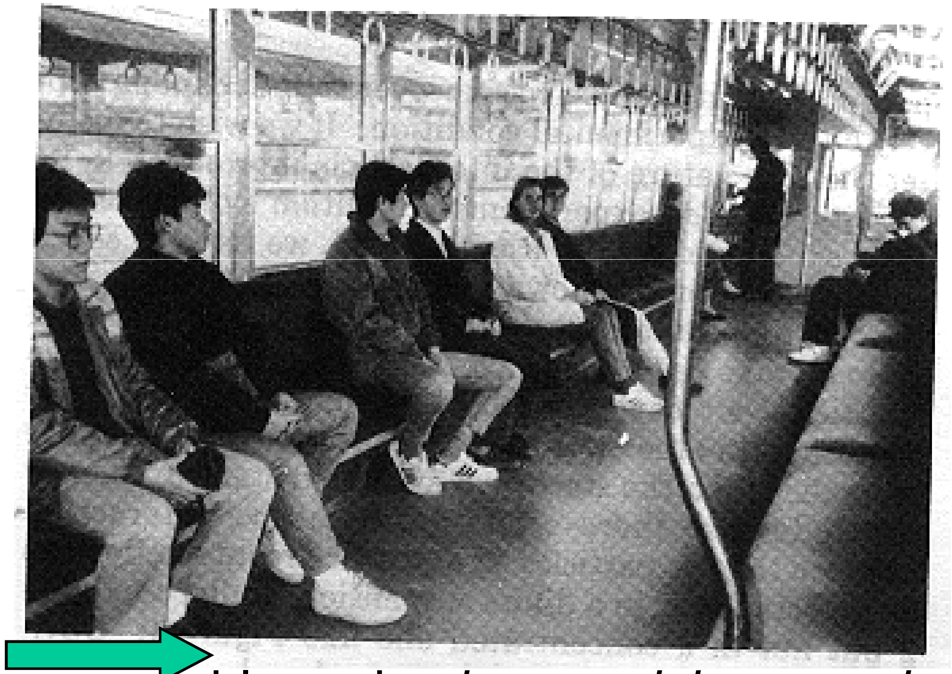
$\rho_\alpha(r)=\rho_\alpha^0 \exp(-v_{eff,\alpha}(r)/kT)$

$v_{eff}(r;\rho) = v(r) + kT\, C^{(1)}(r;\rho);\quad kTC^{(1)}(r;\rho) = (\delta F_{ex}[\rho]/\delta\rho)$

Interparticle correlations

Hell on Wheels for Commuters: Highly Concentrated Dispersed System

Short range correlation



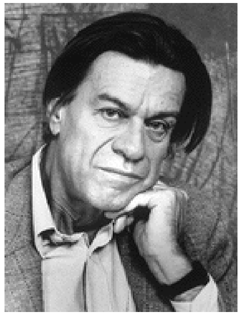
“Dilute Dispersed System”.

Long range correlation

On the right hand side, free seats are available and *solute particles can sit in the free seats. Most solute particles, however, sit voluntarily on the left hand side. This indicates some kind of correlations (attractive here) between the solute particles.*

From HARD MATTER to SOFT MATTER:

MICROSCOPIC ELECTRON DENSITY
to
MESOSCOPIC NUMBER DENSITY



Soft Matter: Applications

- Nanoparticle synthesis using micelles as template
- Chemical reactions under confinement in micelles
- Nanoparticle Assembly: Nucleation
- Interface of chemistry, physics, biology, chemical engineering, materials science

- “Soft matter is the stuff that lies on the borderline between liquid and solid, the stuff that makes the difference between a skeleton and a human being.”

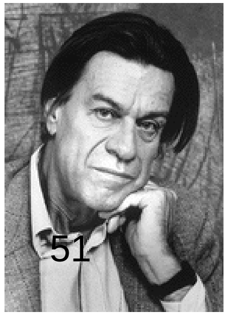
- “Soft matter can be transformed by weak external actions, much as a sculptor deforms the shape of clay by the gentle pressure of a thumb.”

  “This is the central and fundamental definition of soft matter.”

- “The word “Soft” has a double meaning. The materials that one is studying lack the rigid structure of crystalline solids, and the analytical tools that one is using lack the mathematical precision of solid state theory.”

- “Soft matter leaves room for unexpected behaviour, and soft analysis leaves room for imaginative ideas.”

“Fragile Objects, Soft Matter, Hard Science, and the Thrill of Discovery”,
by P.G. de Gennes & J. Badoz (Springer-Verlag, 1996)



SOFT MATTER

Examples & Applications

- Colloidal dispersions, Surfactant assemblies, Liquid crystals, Polymers, Membranes, Emulsions, Gels, Coulombic fluids, Smart fluids, Biological fluids

- Industrial & down to earth applications in day to day life coatings, diapers, drug delivery etc,

- Template in nanoparticle synthesis

Unusual Features

- Weak interaction ~ thermal energy
- Highly compressibile & deformable: Colloidal crystals have shear modulus ~12 orders of magnitude smaller than atomic crystals.
- Paint: At high shear rate, low viscosity: Makes it easy to paint the walls.
- Complexity & Richness in structure & dynamics

Density based approach to Soft Condensed Matter

Various levels of complexity:

- neutral liquid: Neutral hard sphere
  - Lennard-Jones interaction
- Ionic fluid: Solute: charged hard spheres
  - Solvent: dielectric continuum
    - neutral hard sphere
    - dipolar hard sphere
- Colloids: Screened Coulomb (DLVO)
- Liquid Crystals: Hard rod anisotropic potential
- Polymer: Hard sphere/harmonic chain

Interfaces: Confinement: Planar walls
Spherical cavity
Cylindrical pore
Potential: (Hard/L-J/ Coulombic potential)

Density based approach to Soft Condensed Matter under Confinement:

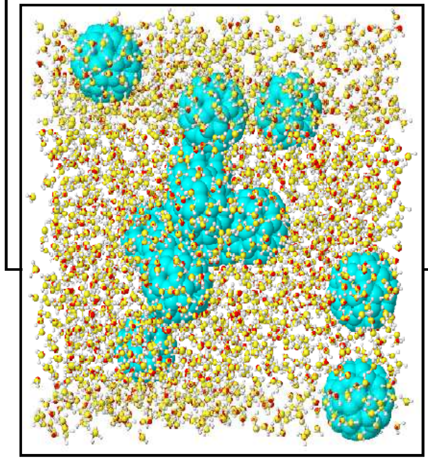
Single Interface: Solid-Liquid Interface

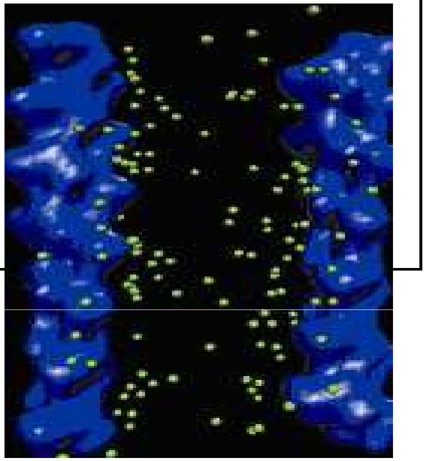
Liquid-Liquid Interface

Liquid-Vapour Interface

Solute-Solvent Interface

(spherical, Cylindrical)

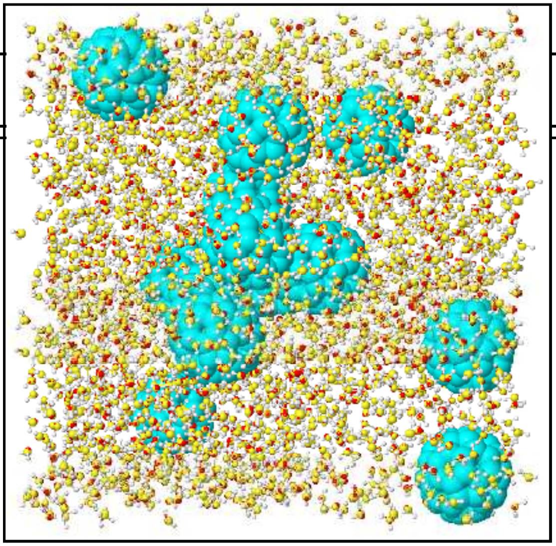




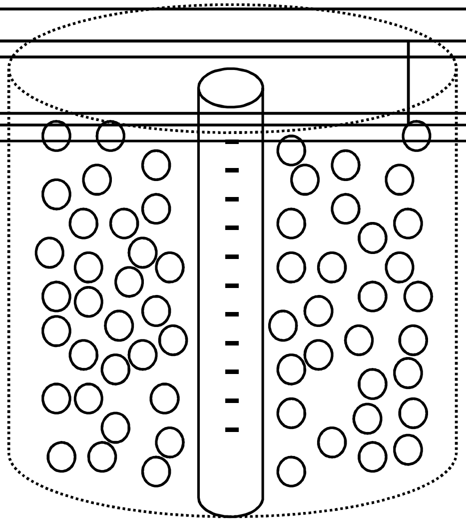
Two Interfaces: Liquid between two plates

Colloid interparticle interaction

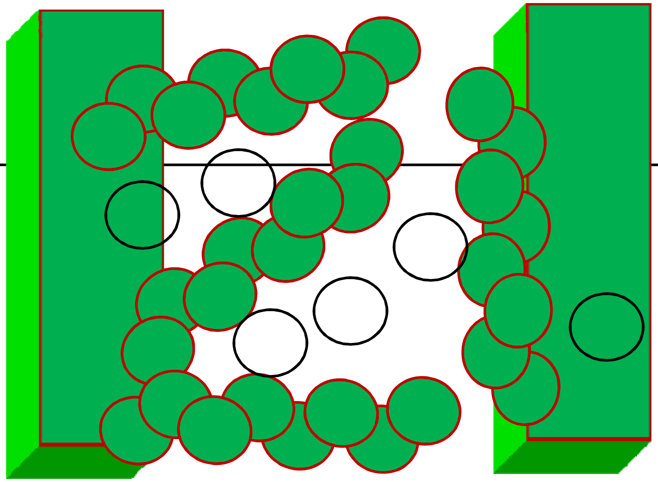
Structure and Dynamics in Condensed Phase



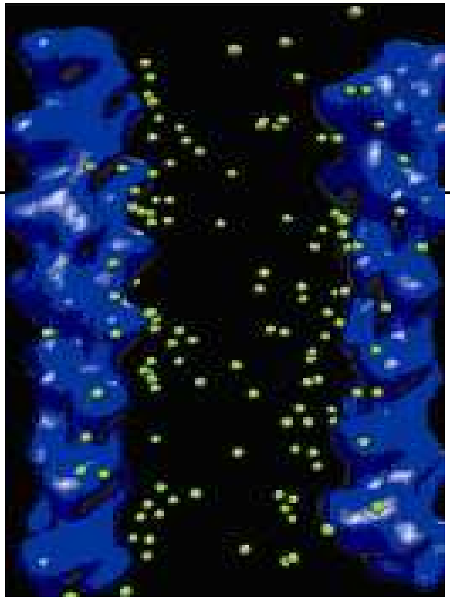
Large molecules in solvent



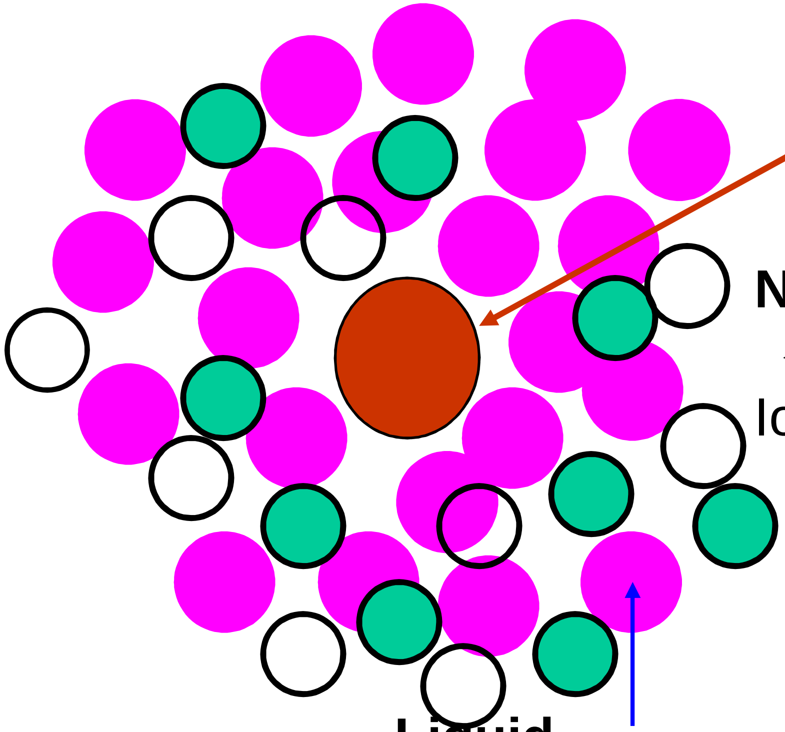
Cylindrical Double Layers



Polymers at Interfaces



Electric Double Layer



Central Particle

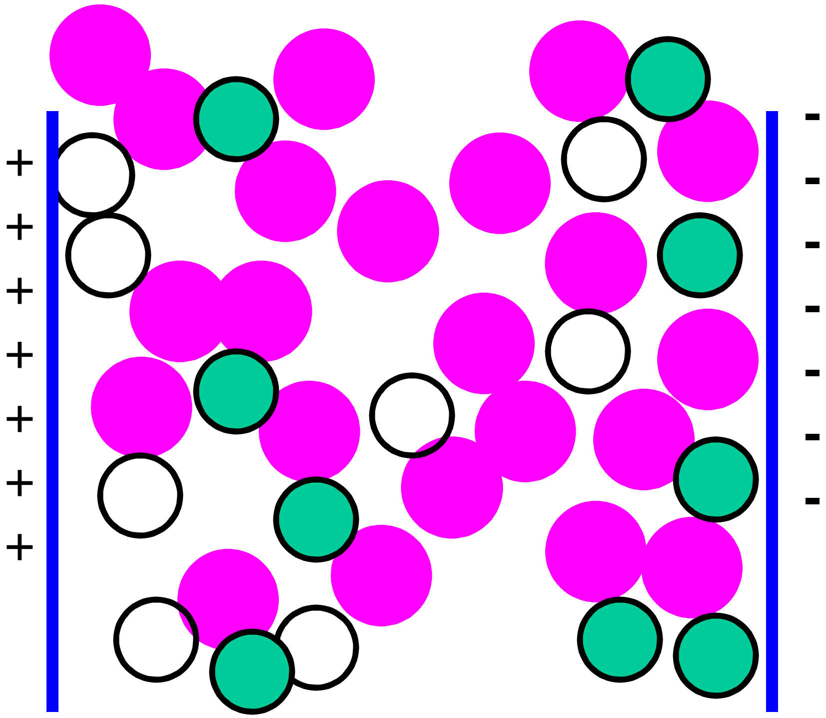
Spherical Geometry

Negative ions

Ion Distribution around a micelle

Positive ions

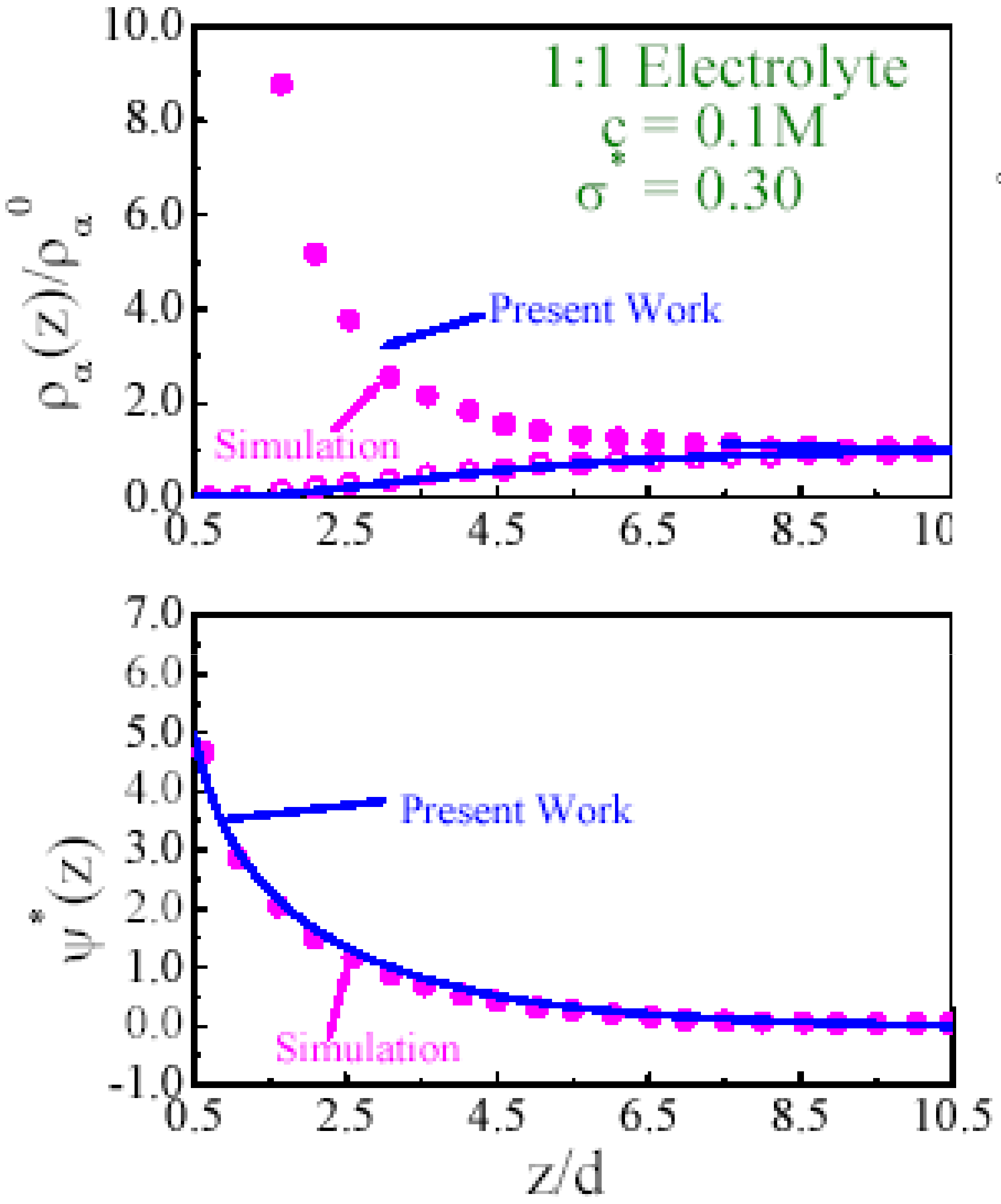
Liquid Particles

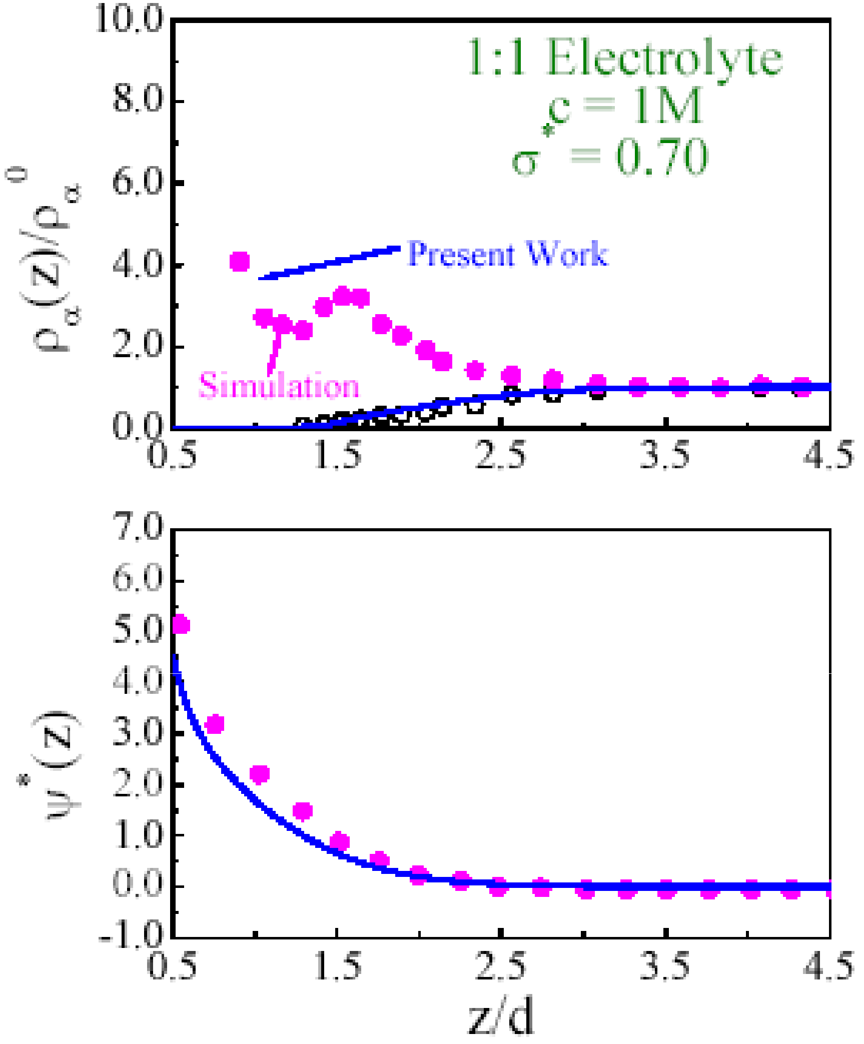


Charged Walls

Planar Geometry

Electrode-Electrolyte Interface

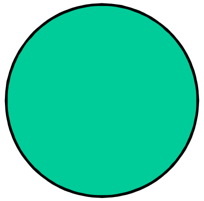




Restricted Primitive Model
Charged hard sphere ions

Liquid-phase synthesis of nanomaterials

Nucleation and growth of particles: Role of supersaturation

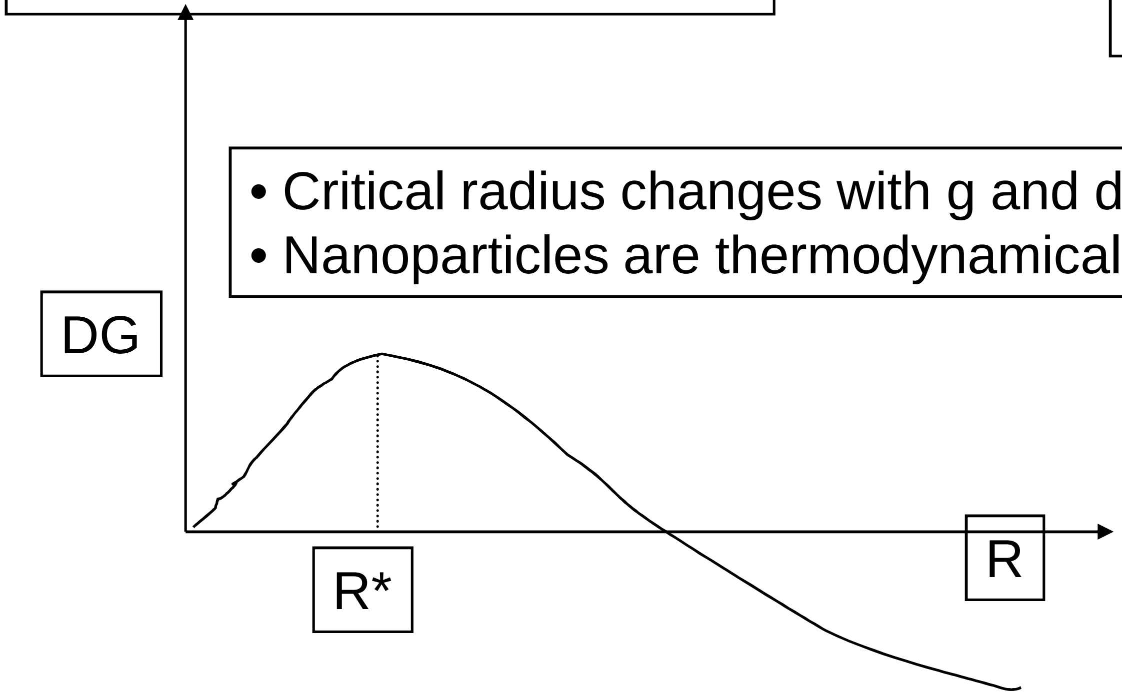


$$DG = - \frac{4 p R^3}{3 v} Dm + 4 p R^2 g$$

Critical radius for nucleation

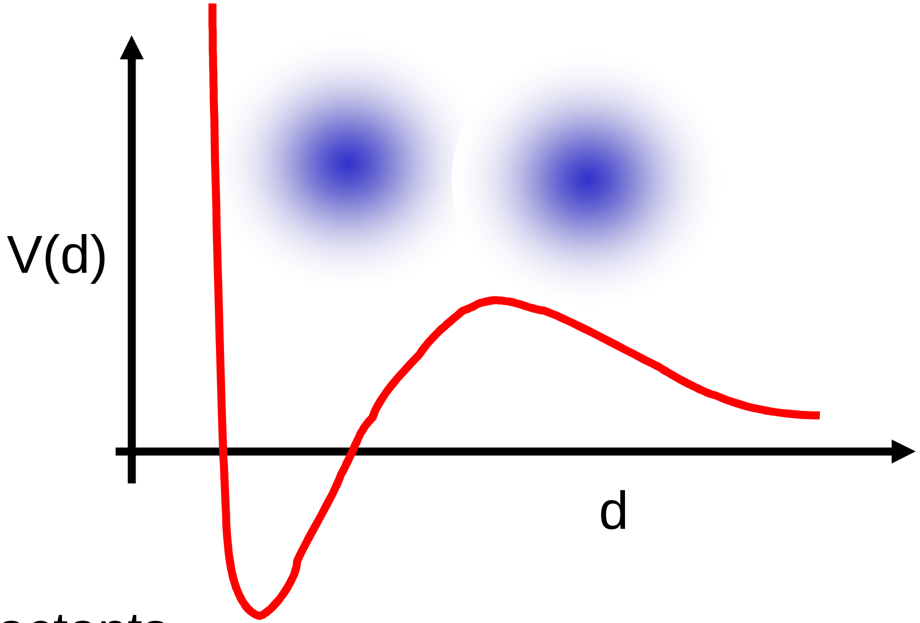
$$R^* = \frac{2 g v}{Dm}$$

- Critical radius changes with g and degree of supersaturation
- Nanoparticles are thermodynamically unstable



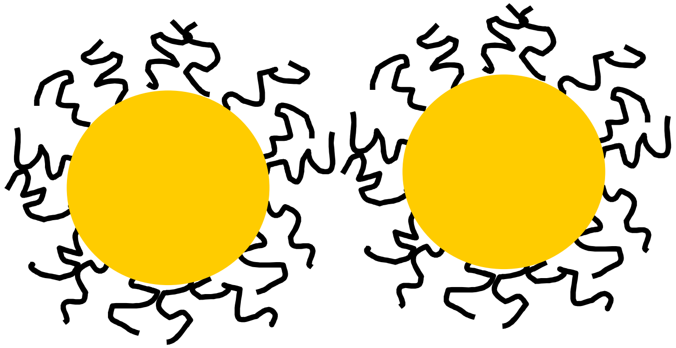
Stabilization of particles

1) Charge Stabilization



2) Steric stabilization

Adsorption/ grafting of polymers or surfactants



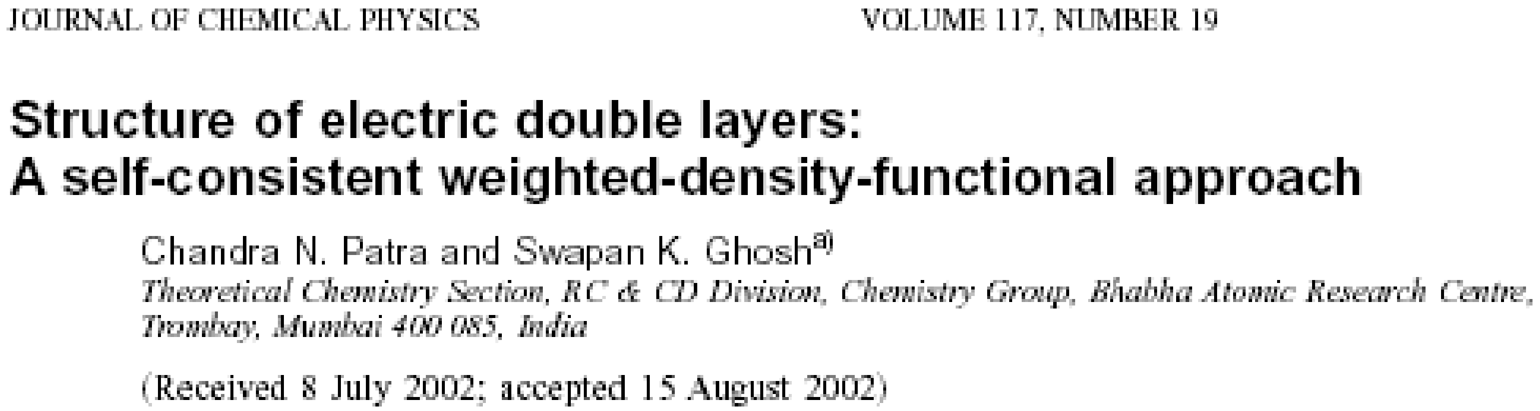
3) Kinetic stabilization

Diffusion controlled growth

Size Distribution of Nanoparticles:

•Use of Templates: Micelles, Microemulsion, etc

•Understanding the mechanism:



JOURNAL OF CHEMICAL PHYSICS VOLUME 117, NUMBER 19 15 NOVEMBER 2002

Structure of electric double layers: A self-consistent weighted-density-functional approach

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(Received 8 July 2002; accepted 15 August 2002)

Earlier theories: Continuum theories
Spherical geometry: Debye-Huckel theory
Planar geometry: Guoy-Chapman theory

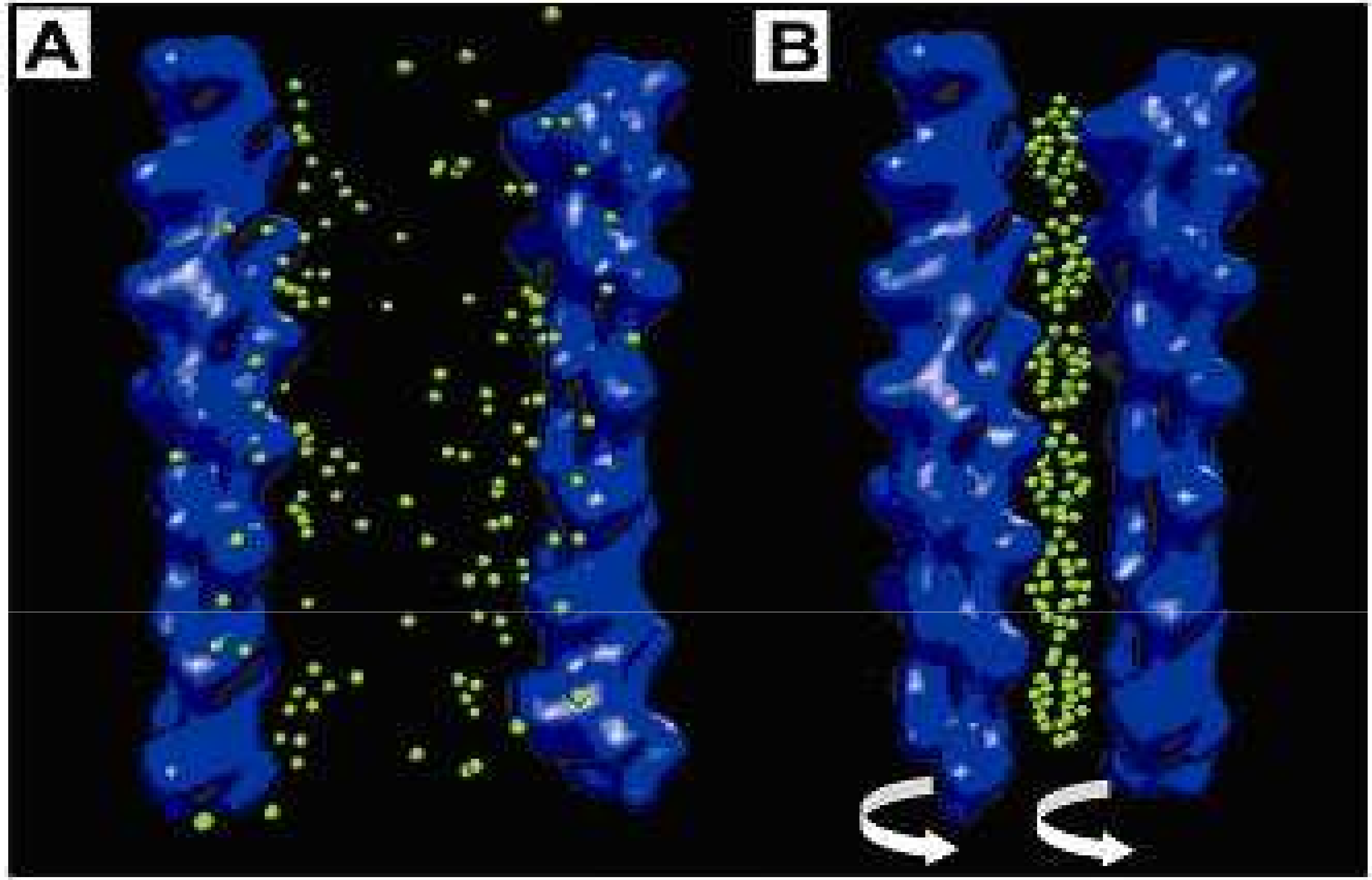
Fail to predict the nonmonotonic structure of ion distribution

Density Functional Theory includes effect of Interparticle correlations (both short and long range)

$\rho_a(r)=\rho_a{}^0 \exp([-v_a(r) + v_{eff}(r)]/kT])$

•Effective potential due to interparticle correlation

$v_{eff}(r) = [C^{(1)}(r;\rho(r))-C^{(1)}(\rho_0)]\, kT$



Schematic representations of uncondensed and condensed F-actin. (A) At low multivalent ion concentrations, two F-actin filaments maintain their native 13/6 symmetry and are unbound. (B) At high multivalent ion concentrations, the ions collectively form a CDW and bundle F-actin filaments.

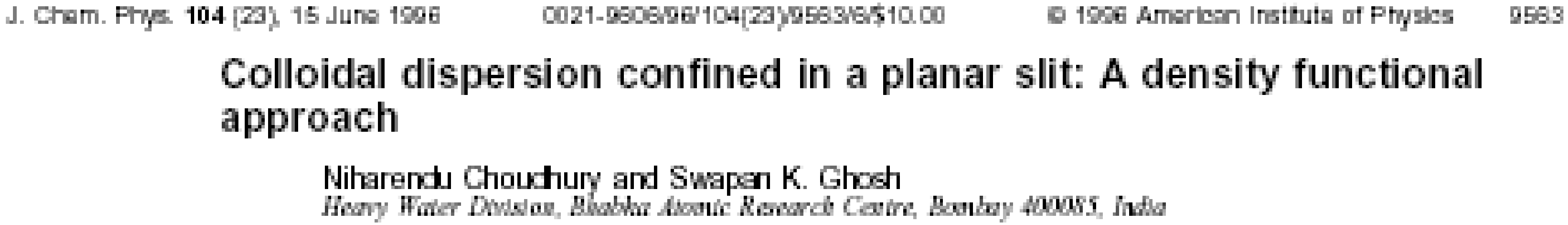
The Attraction of Like Charges

- Strands of actin protein clump together in water--even though they are all negatively charged--as long as the right ions are dissolved in the solution.

- Many large biological molecules like DNA seem to flout a basic law of nature--although their charges have same sign, they can attract one another and clump together in water.

- The explanation lies with dissolved ions--charged atoms or small molecules--that somehow cancel the large molecules' charges, but the details have been unclear because not all ions, and not all sizes work.

IMPORTANT: Charge Inversion in electric double layer
can explain the attraction of like charges.
(analogy to binding of two positively charged
nuclei in molecules)



J. Chem. Phys. 104 (23), 15 June 1996 0021-9606/96/104(23)/9563/6/$10.00 © 1996 American Institute of Physics 9563

Colloidal dispersion confined in a planar slit: A density functional approach

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JOURNAL OF CHEMICAL PHYSICS VOLUME 111, NUMBER 4 22 JULY 1999

Colloidal suspensions in charged cylindrical pores: A perturbative density functional approach

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Theoretical Chemistry Section, RC & CD Division, Chemistr
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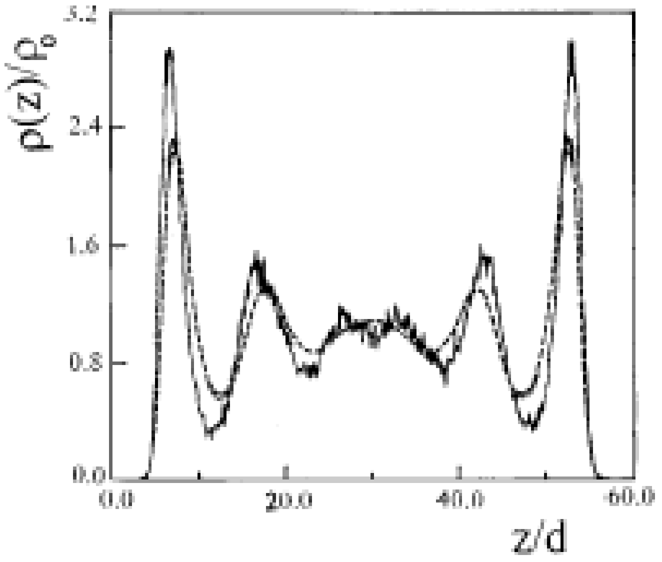
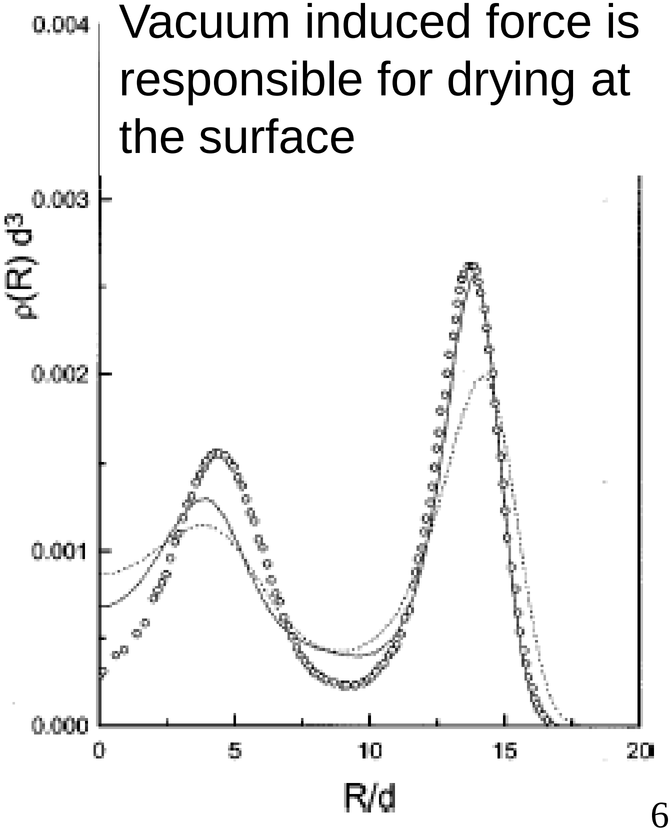


FIG. 3. Plot of the density profile $\rho(z)/\rho_0$ vs z/d for a model colloidal suspension for wall separation of 60d. The parameters and the key are same as in Fig. 1.

Vacuum induced force is responsible for drying at the surface



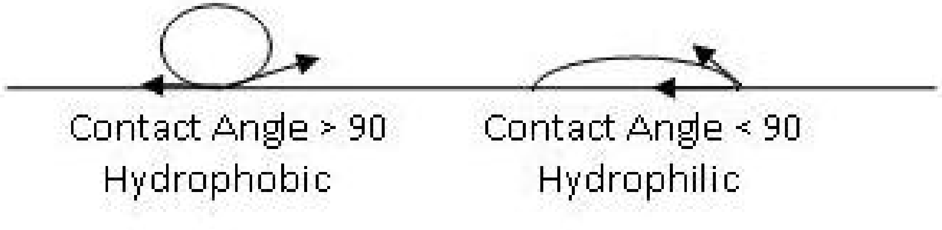
Hydrophobicity & the Lotus Effect
Hydrophobic vs. Hydrophilic

water

hydrophobic surface

water

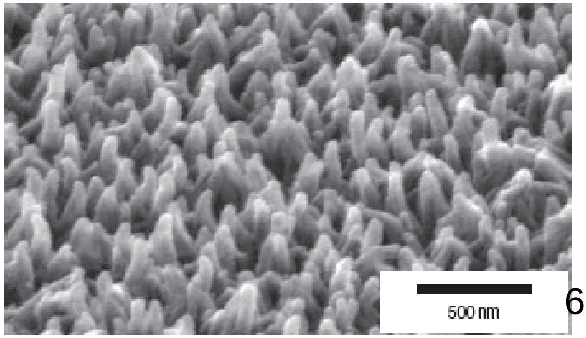
hydrophilic surface



air

water

nano-roughened surface



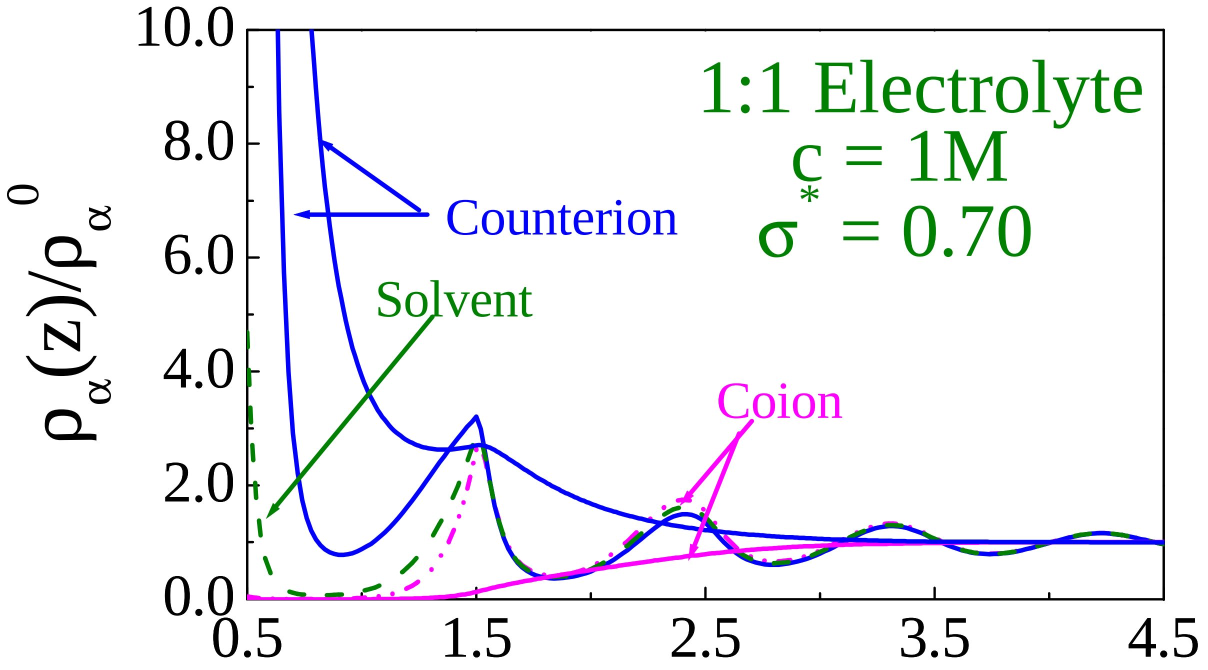
PHYSICAL REVIEW E VOLUME 48, NUMBER 2 AUGUST 1993

Weighted-density-functional theory of electrode-electrolyte interface: Beyond the primitive model

Chandra N. Patra and Swapan K. Ghosh
Heavy Water Division, Bhabha Atomic Research Centre, Bombay 400085, India

(Received 23 December 1992; revised manuscript received 19 April 1993)

Effect of Finite size of the solvent molecules



THE JOURNAL OF CHEMICAL PHYSICS **129**, 154906 (2008)

Structure of cylindrical electric double layers: A systematic study by Monte Carlo simulations and density functional theory

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Theoretical Chemistry Section, Chemistry Group, Bhabha Atomic Research Centre,
Mumbai 400 085, India

(Received 28 April 2008; accepted 9 S

We present a systematic study of th
distribution of small ions around a cyli
and density functional theory. The polyi
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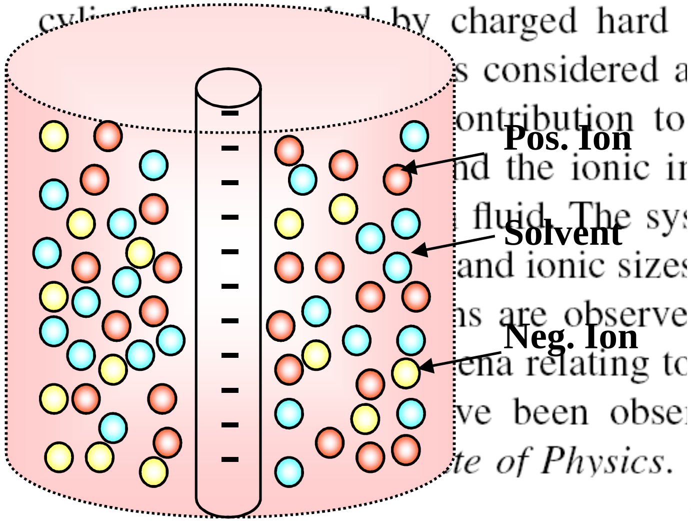


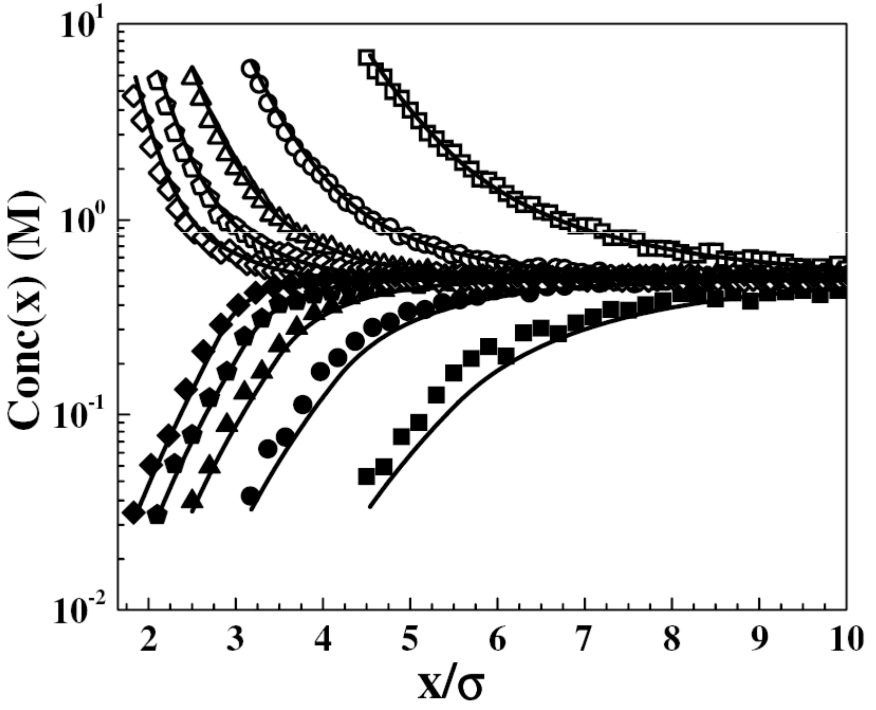
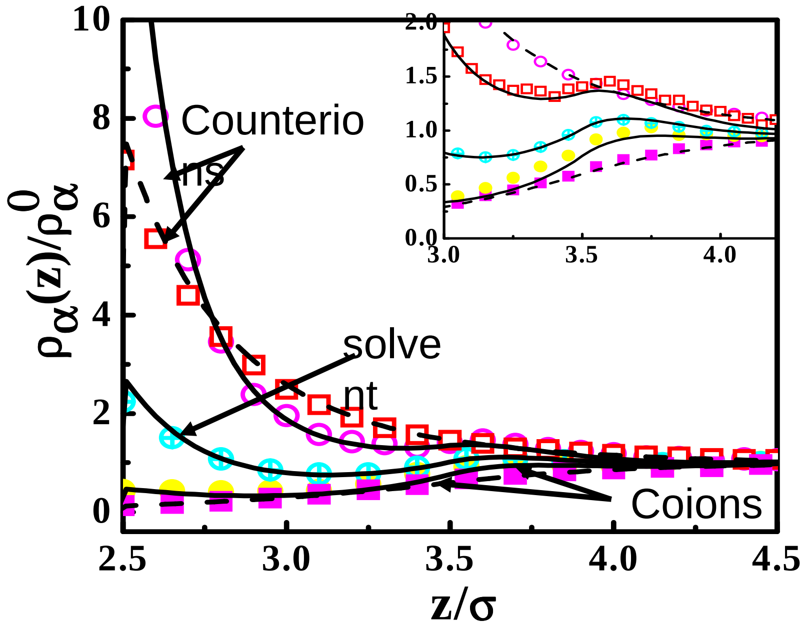
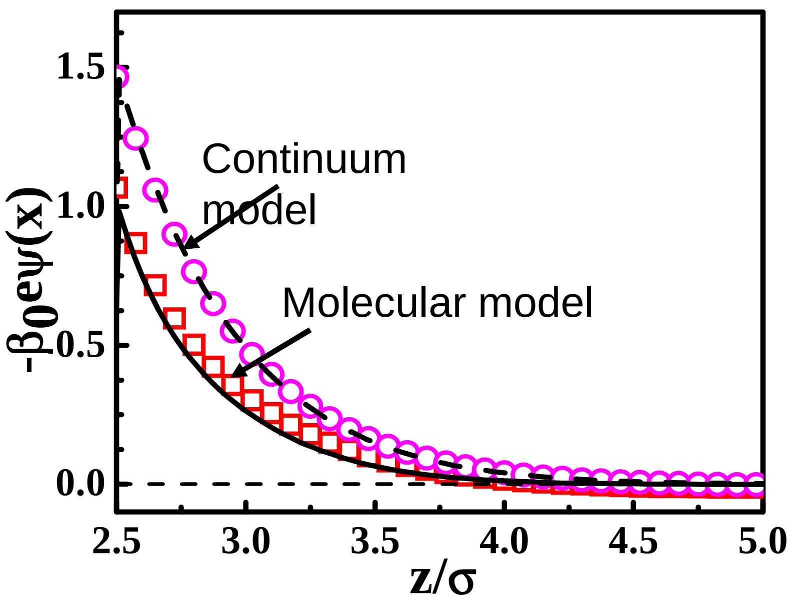


FIG. 7. Ionic concentration profiles for the 1:1 salt (NaCl) for 500 mM concentration with varying sizes of small ions. Symbols □, ○, △, open pentagon, and ◇, represent σ=2, 3, 4, 5, and 6 Å, respectively. The key is the same as in Fig. 1.

Density profiles



Mean electrostatic profiles

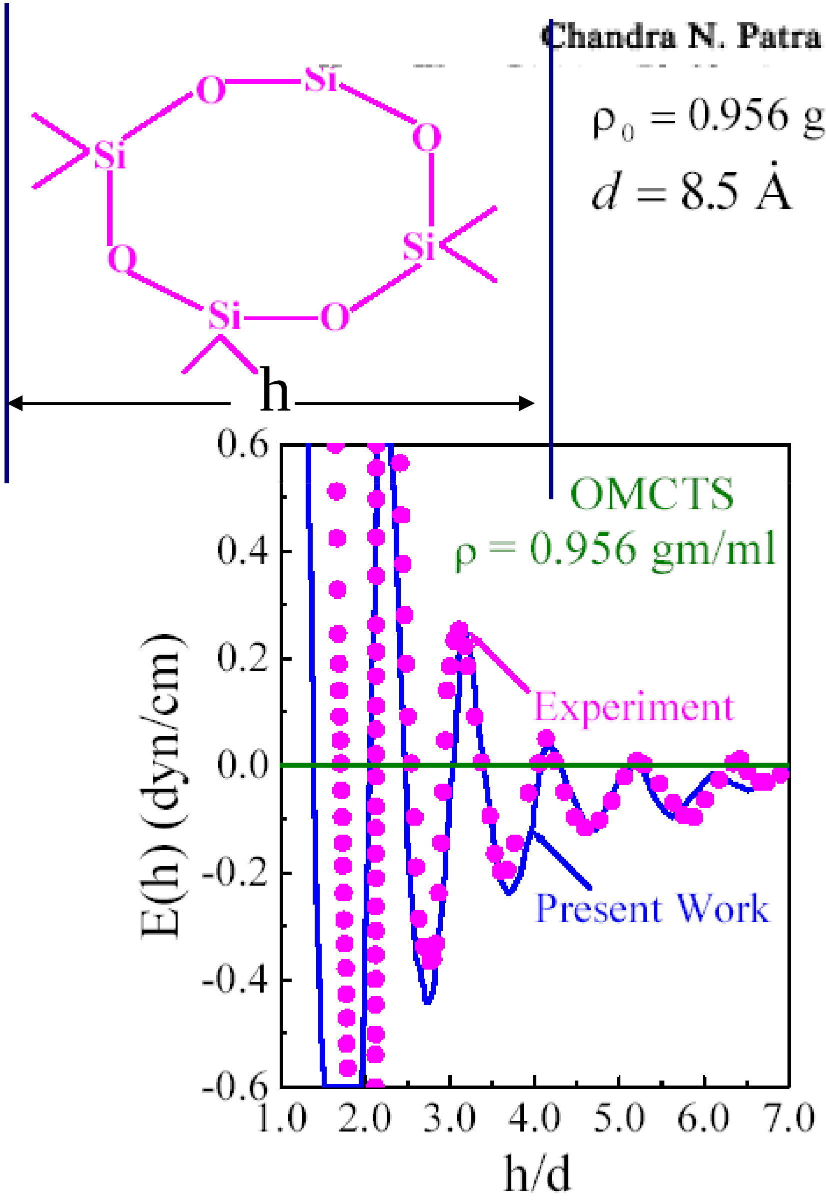


- ➢ Counterions show layering at the surface and co-ions are depleted from the surface
- ➢ Layering occurs due to interplay of electrostatic attractions from polyion, the interionic correlations and the hard-core exclusion by the polyion and the small ions
- ➢ Oscillatory behavior of the density distribution is well predicted from DFT
- ➢ Molecular solvent induces more oscillations in density profiles due to excluded volume effects
- ➢ Mean electrostatic potential also show decreased magnitude in presence of molecular solvent due to excluded volume effects
- ➢ DFT (lines) results are in better agreement with simulations (symbols)

PHYSICAL REVIEW E VOLUME 50, NUMBER 6 DECEMBER 1994

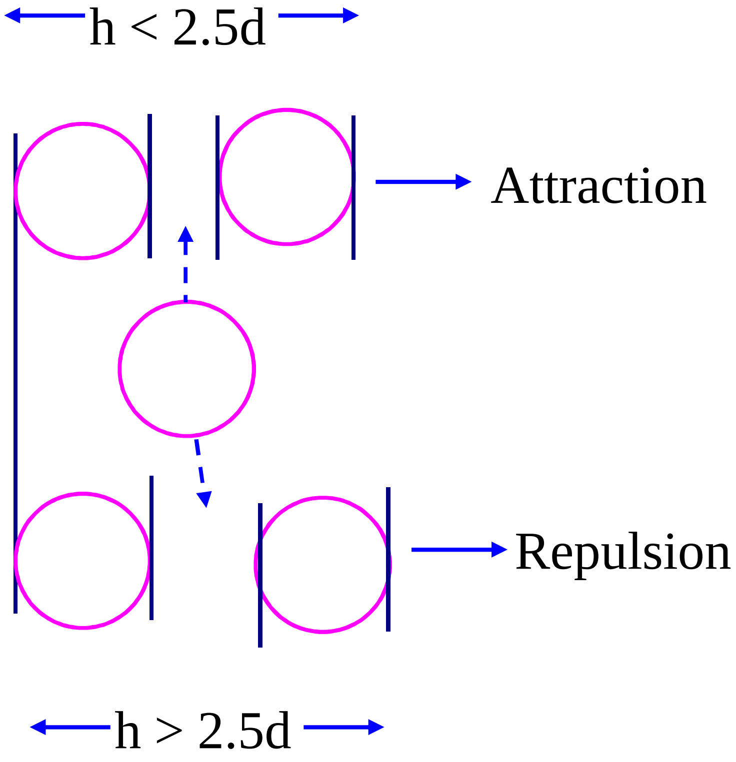
Density functional approach to solvent-induced interactions in neutral liquids: Comparison with experimental results

Chandra N. Patra and Swapan K. Ghosh



$\rho_0 = 0.956$ gm / ml

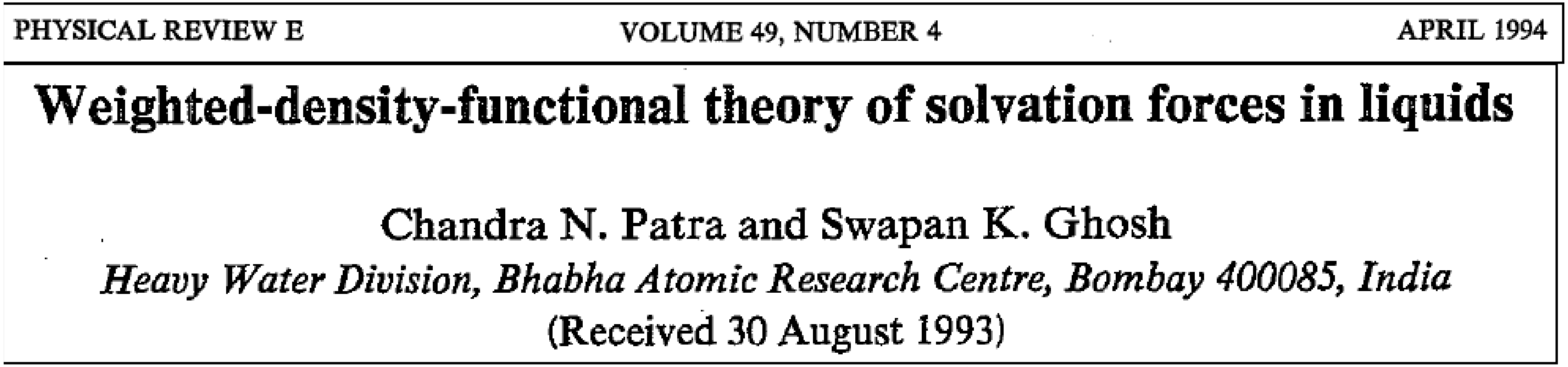
$d = 8.5$ Å


h < 2.5d

Attraction

Repulsion

h > 2.5d



PHYSICAL REVIEW E VOLUME 49, NUMBER 4 APRIL 1994

Weighted-density-functional theory of solvation forces in liquids

Chandra N. Patra and Swapan K. Ghosh
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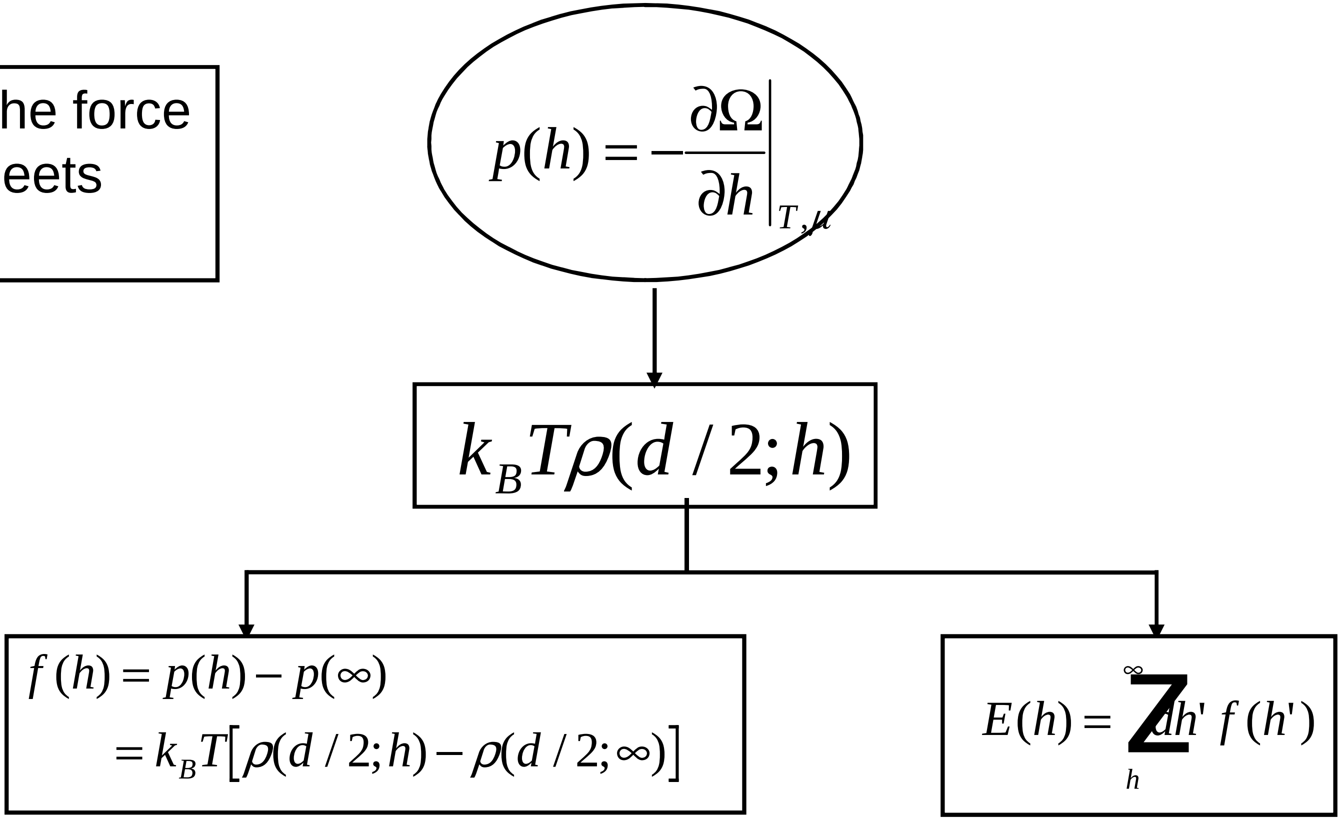
(Received 30 August 1993)

Oscillating nature of the force
Between two mica sheets
Confining a liquid



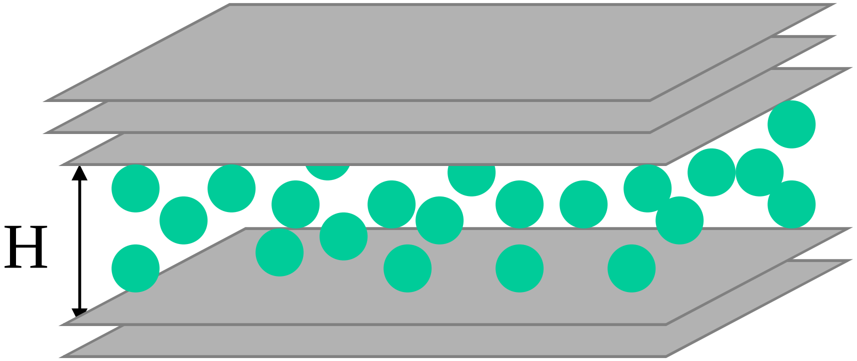
$$p(h) = -\left.\frac{\partial\Omega}{\partial h}\right|_{T,\mu}$$

$$k_B T \rho(d/2; h)$$

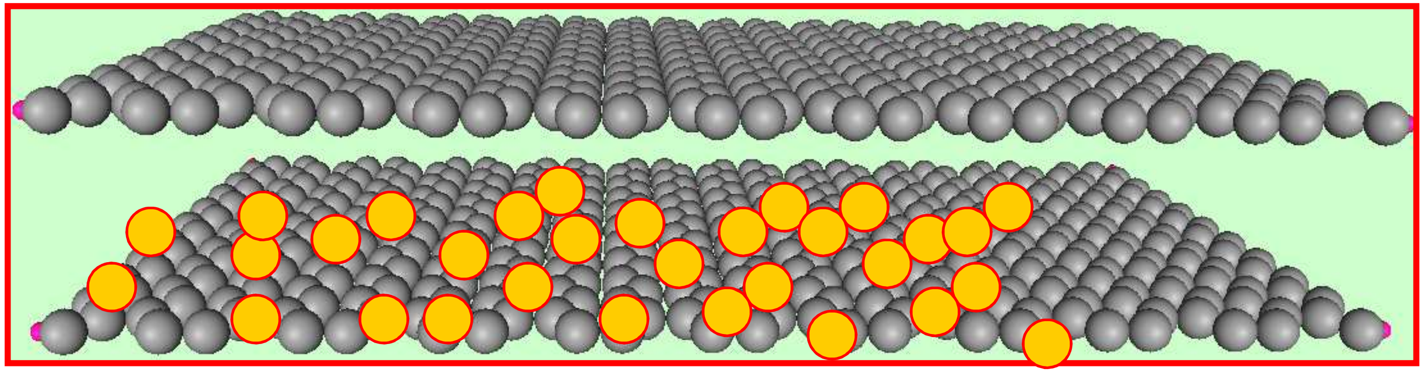
$$\begin{aligned} f(h) &= p(h) - p(\infty) \\ &= k_B T\left[\rho(d/2; h) - \rho(d/2; \infty)\right] \end{aligned}$$

$$E(h) = \int_h^\infty dh'\, f(h')$$

Fluids inside planar Nanopores



Slit shaped “micropores



Adsorption in Nanopores

PHYSICAL REVIEW E, VOLUME 64, 021206

Adsorption of Lennard-Jones fluid mixture in a planar slit: A perturbative density functional approach

Niharendu Choudhury and Swapan K. Ghosh
Theoretical Chemistry Section, RC and CD Division, Chemistry Group, Bhabha Atomic Research Centre, Mumbai 400 085, India

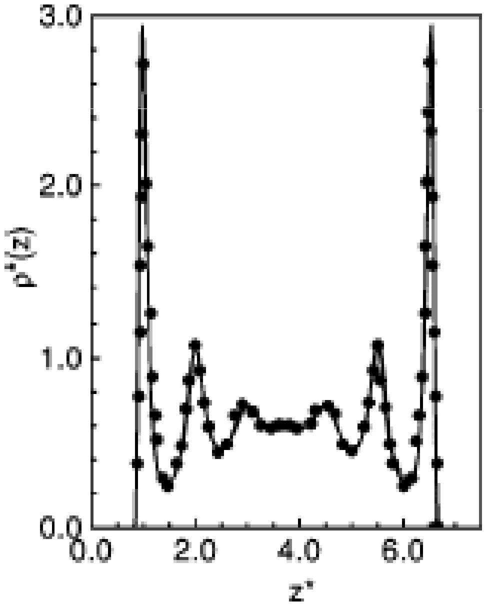
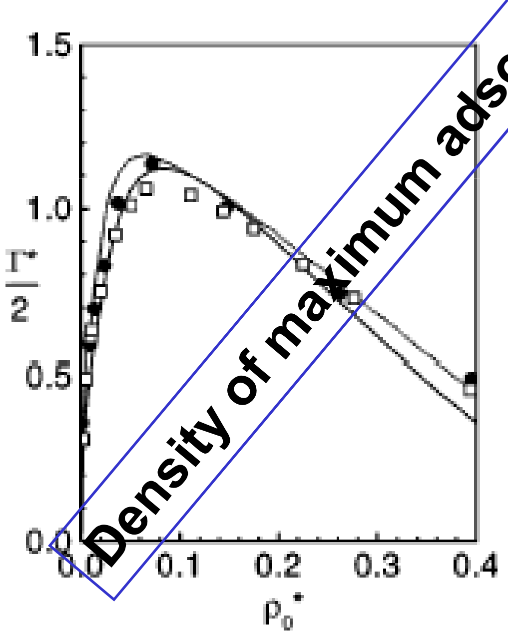
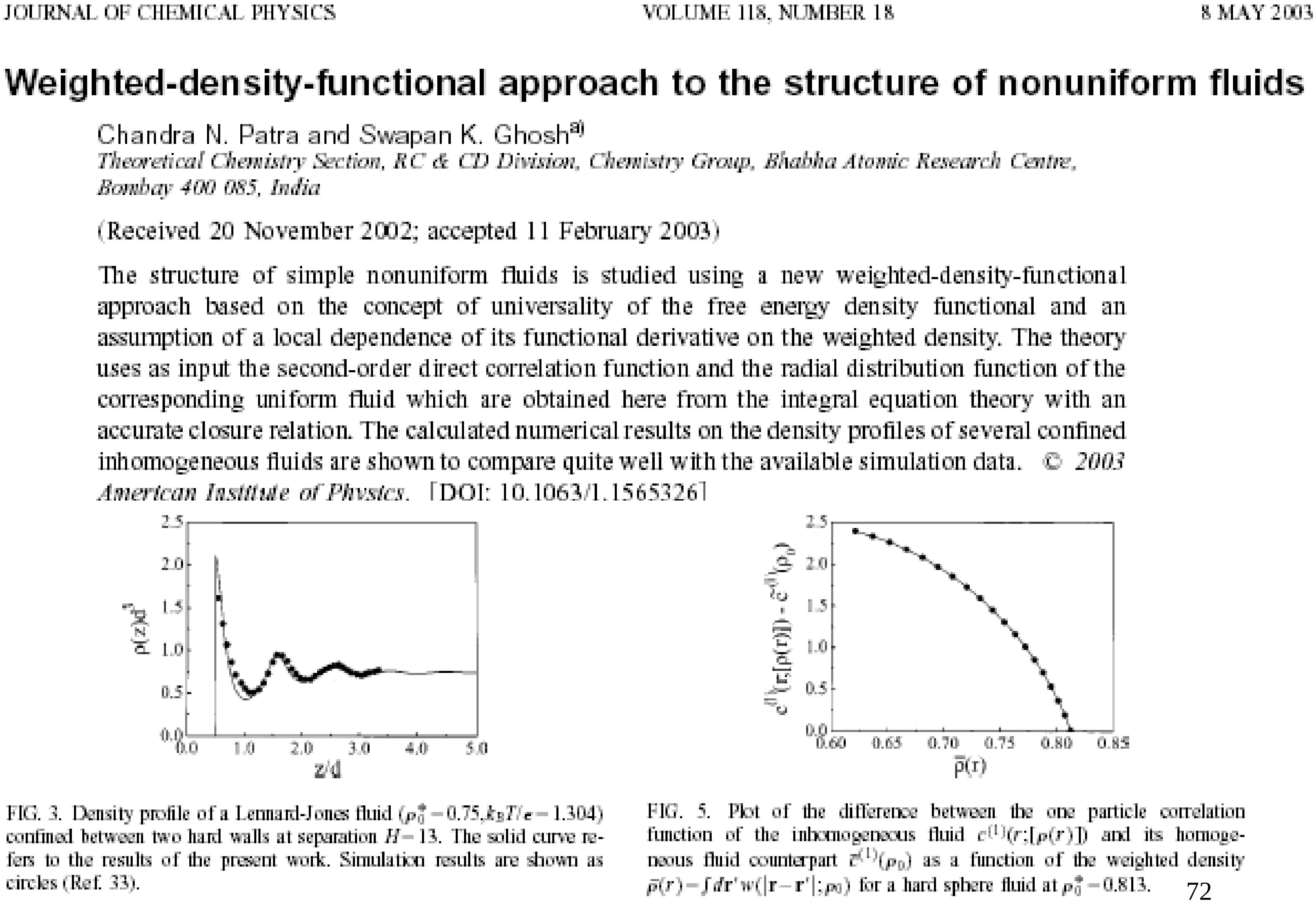


FIG. 4. Plot of density profiles $\rho^*(z)$ vs z^* for a pure Lennard-Jones fluid of bulk density $\rho_0^* = 0.5925$ in a planar slit of of width $H^* = 7.5$ at $T^* = 1.20$. The key is the same as in Fig. 2. Simulation results are taken from Ref. [44].



Density of maximum adsorption

FIG. 6. Plot of excess adsorption isotherm per unit area Γ^* vs ρ_0^* of ethylene in carbon slit pore of width $H^* = 5$ at $T^* = 1.35$. The key is the same as in Fig. 2. Simulation results that are shown as circles are taken from Ref. [35(a)] (also reproduced in Ref. [39(a)]) and those shown as open squares are taken from Ref. [41].



JOURNAL OF CHEMICAL PHYSICS VOLUME 118, NUMBER 18 8 MAY 2003

Weighted-density-functional approach to the structure of nonuniform fluids

Chandra N. Patra and Swapan K. Ghosh[a)]
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(Received 20 November 2002; accepted 11 February 2003)

The structure of simple nonuniform fluids is studied using a new weighted-density-functional approach based on the concept of universality of the free energy density functional and an assumption of a local dependence of its functional derivative on the weighted density. The theory uses as input the second-order direct correlation function and the radial distribution function of the corresponding uniform fluid which are obtained here from the integral equation theory with an accurate closure relation. The calculated numerical results on the density profiles of several confined inhomogeneous fluids are shown to compare quite well with the available simulation data. [DOI: 10.1063/1.1565326]

FIG. 3. Density profile of a Lennard-Jones fluid ($\rho_0^* = 0.75, k_BT/\epsilon = 1.304$) confined between two hard walls at separation $H = 13$. The solid curve refers to the results of the present work. Simulation results are shown as circles (Ref. 33).

FIG. 5. Plot of the difference between the one particle correlation function of the inhomogeneous fluid $c^{(1)}(r;[\rho(r)])$ and its homogeneous fluid counterpart $\bar{c}^{(1)}(\rho_0)$ as a function of the weighted density $\bar{\rho}(r) = \int d\mathbf{r}' w(|\mathbf{r}-\mathbf{r}'|;\rho_0)$ for a hard sphere fluid at $\rho_0^* = 0.813$.

PHYSICAL REVIEW E **66**, 012501 (2002)

Simple weighted density functional approach to the structure of polymers at interfaces

Chandra N. Patra and Swapan K. Ghosh*
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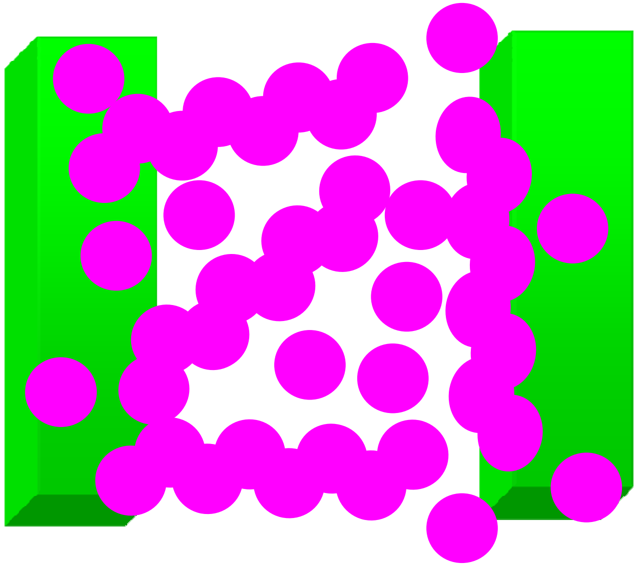
(Received 2 January 2002; revised manuscript received 19 April 2002; published 24 July 2002)



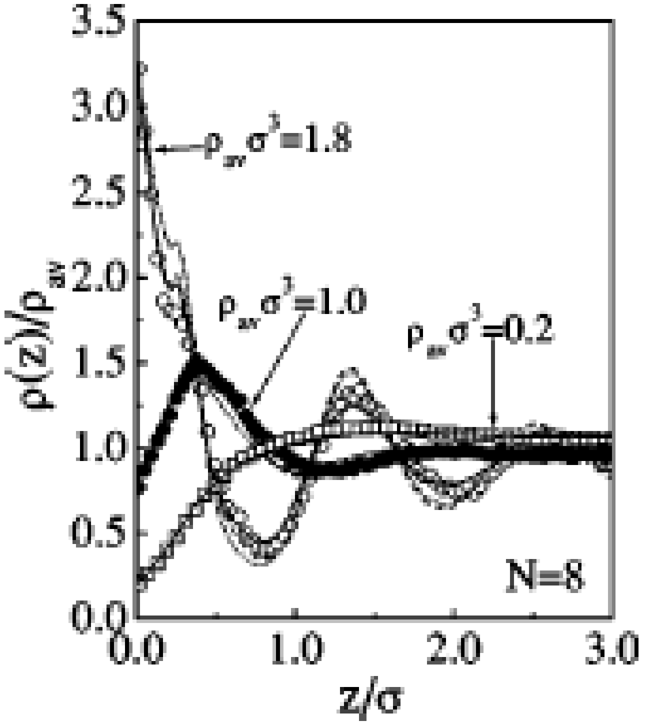


FIG. 1. Density profiles of 8-mers at $\rho_{av}\sigma^3 = 0.2$, 1.0, and 1.8. Present work (——); YW theory [9] (- - - - - -); Yethiraj [10] (— — —). Circles represent Monte Carlo simulations.

J. Chem. Phys. **104** (23), 15 June 1996 0021-9606/96/104(23)/9563/6/$10.00 © 1996 American Institute of Physics 9563

Colloidal dispersion confined in a planar slit: A density functional approach

Niharendu Choudhury and Swapan K. Ghosh
Heavy Water Division, Bhabha Atomic Research Centre, Bombay 400085, India

(Received 26 October 1995; accepted 7 March 1996)

We present a simple density functional approach for the prediction of the local density profile of a colloidal suspension confined in a charged planar slit. Both the interparticle and wall–particle interactions are modeled to be of screened Coulomb type. The short range part of the interparticle correlation is treated through a nonperturbative weighted density approach, while the long range contribution is treated perturbatively in terms of the density inhomogeneity. The input correlation functions for the bulk fluid are obtained through the rescaled mean spherical approximation. The calculated density profiles are shown on an average to compare well with results from computer simulation. © *1996 American Institute of Physics.* [S0021-9606(96)51222-5]

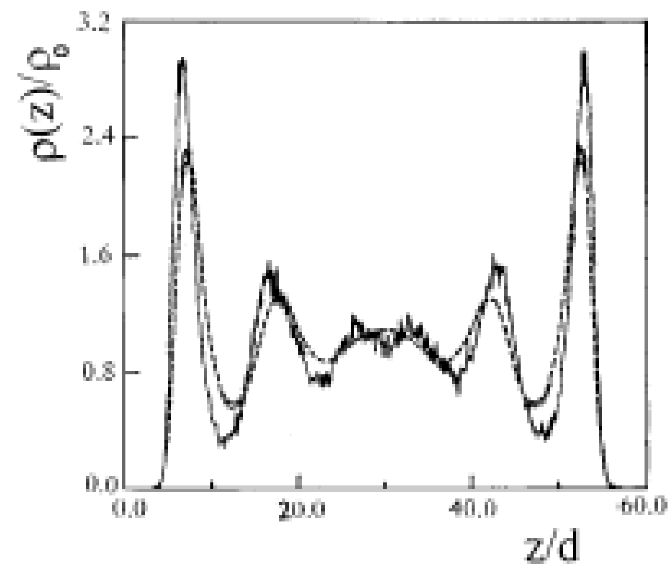


FIG. 3. Plot of the density profile $\rho(z)/\rho_0$ vs z/d for a model colloidal suspension for wall separation of 60*d*. The parameters and the key are same as in Fig. 1.

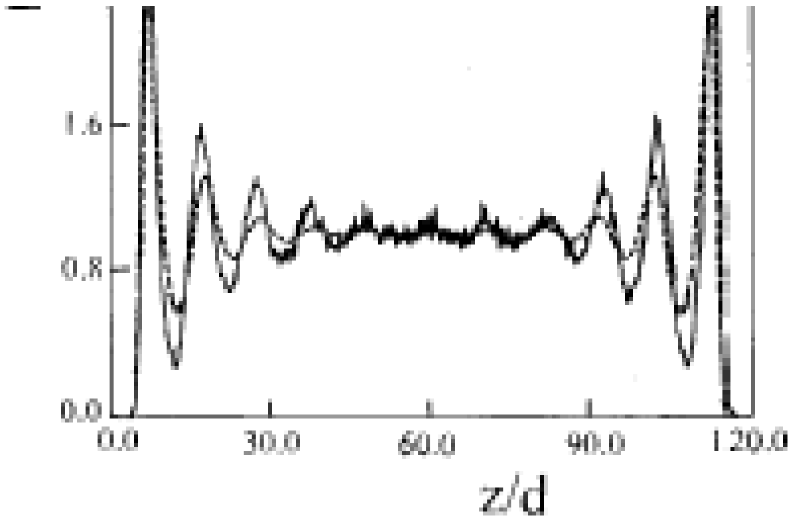
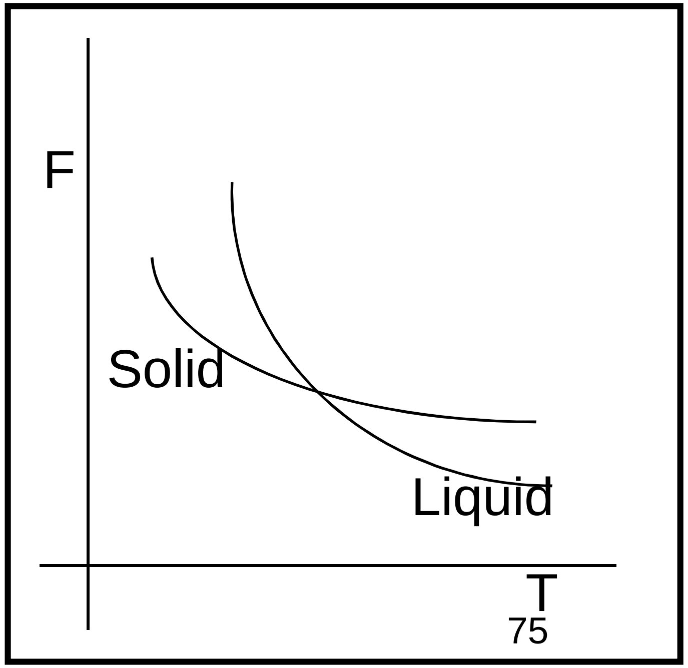


FIG. 4. Plot of the density profile $\rho(z)/\rho_0$ vs z/d for a model colloidal suspension for wall separation of 120*d*. The parameters and the key are same as in Fig. 1.

Density Functional Theory of Freezing

- So far, examples of inhomogeneous density caused by the field of external potential
- Spontaneous appearance of inhomogeneous density as a function of control parameter
- Examples of freezing as a function of temperature or density

- Free energy of the homo-geneous liquid phase and the inhomogeneous solid phase obtained as density functionals
- The point of crossing indicates phase transition



PHYSICAL REVIEW E **VOLUME 57, NUMBER 2** **FEBRUARY 1998**

Modified weighted density-functional approach to the crystal-melt interface

Niharendu Choudhury and Swapan K. Ghosh
Heavy Water Division, Bhabha Atomic Research Centre, Bombay 400085, India

(Received 31 July 1997)

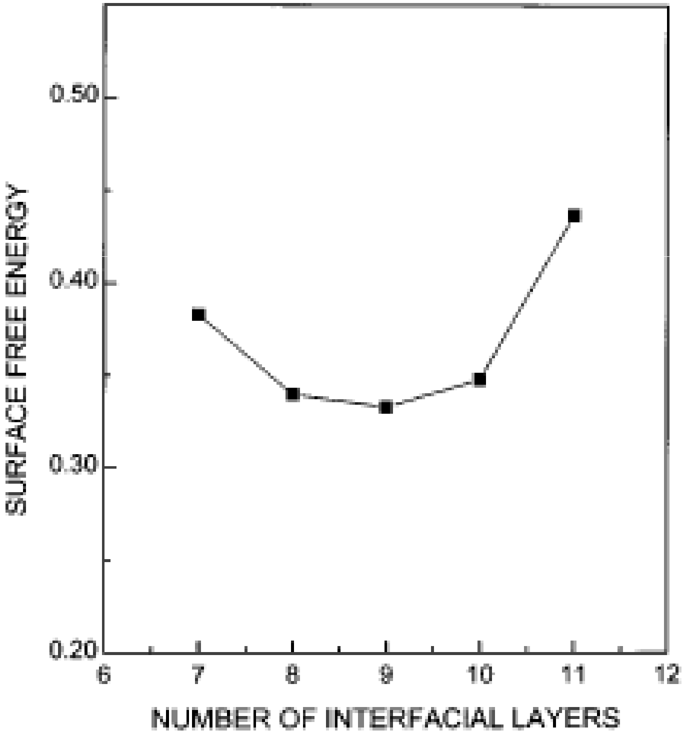


FIG. 1. Plot of calculated surface free energy vs number of interfacial layers for fcc liquid (111) interface of hard sphere fluid.

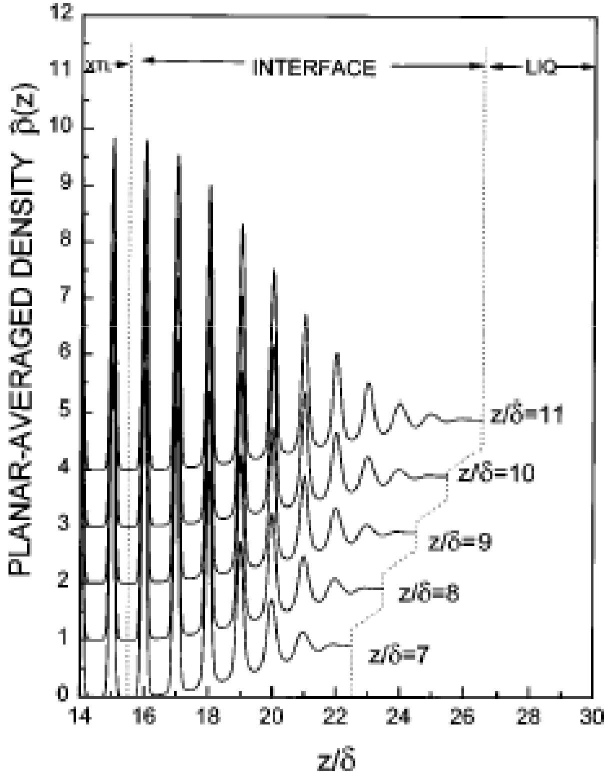


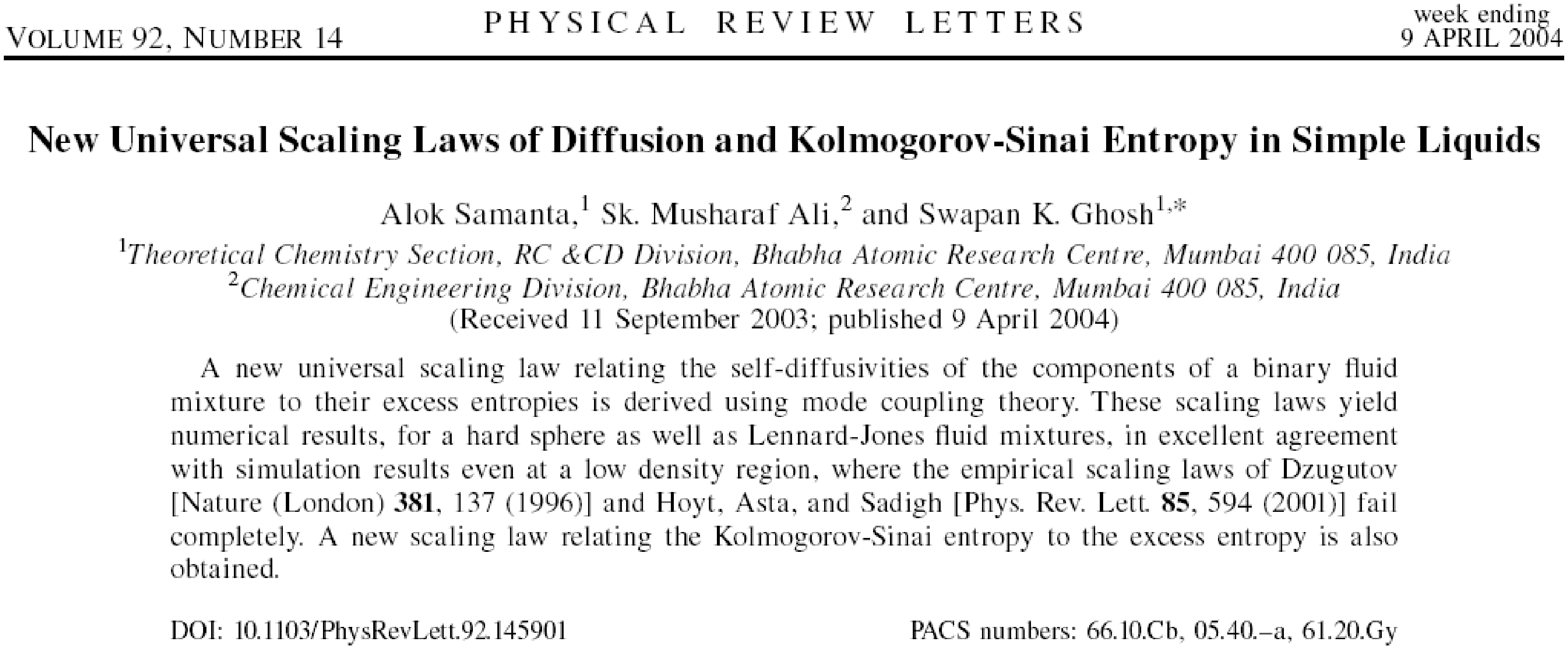
FIG. 2. Plot of planar averaged interfacial density profile $\hat{\rho}(z)$ for the (111) fcc liquid interface of hard sphere fluid for several values of interfacial width.

Diffusion in Fluid Mixtures

- Diffusion is an important dynamical phenomenon for chemical reactions & other processes in condensed phase

- Difficulty in theoretical evaluation due to lack of knowledge of various dynamical correlation Functions

- Relationship between the transport coefficients and structural properties has remained as one of the most challenging and non-trivial tasks in the field of condensed phase dynamics.



VOLUME 92, NUMBER 14 PHYSICAL REVIEW LETTERS week ending 9 APRIL 2004

New Universal Scaling Laws of Diffusion and Kolmogorov-Sinai Entropy in Simple Liquids

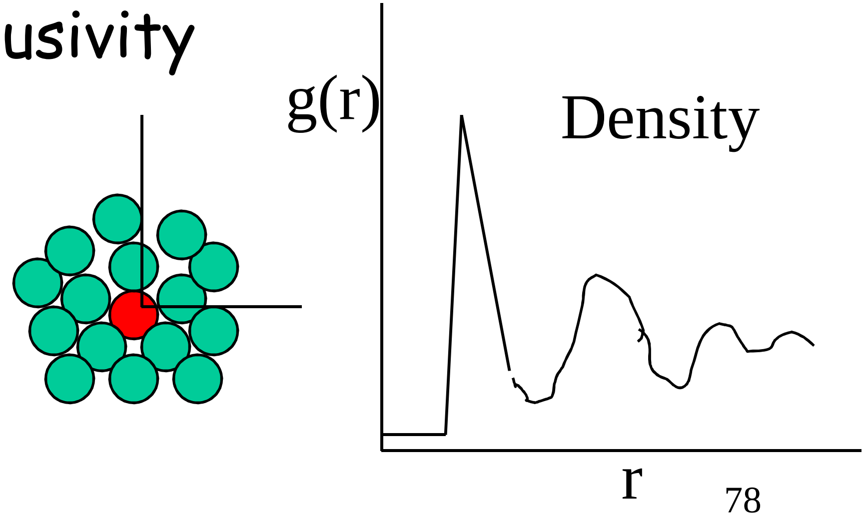
Alok Samanta,[1] Sk. Musharaf Ali,[2] and Swapan K. Ghosh[1,*]
[1] *Theoretical Chemistry Section, RC &CD Division, Bhabha Atomic Research Centre, Mumbai 400 085, India*
[2] *Chemical Engineering Division, Bhabha Atomic Research Centre, Mumbai 400 085, India*

(Received 11 September 2003; published 9 April 2004)

A new universal scaling law relating the self-diffusivities of the components of a binary fluid mixture to their excess entropies is derived using mode coupling theory. These scaling laws yield numerical results, for a hard sphere as well as Lennard-Jones fluid mixtures, in excellent agreement with simulation results even at a low density region, where the empirical scaling laws of Dzugutov [Nature (London) **381**, 137 (1996)] and Hoyt, Asta, and Sadigh [Phys. Rev. Lett. **85**, 594 (2001)] fail completely. A new scaling law relating the Kolmogorov-Sinai entropy to the excess entropy is also obtained.

DOI: 10.1103/PhysRevLett.92.145901 PACS numbers: 66.10.Cb, 05.40.–a, 61.20.Gy

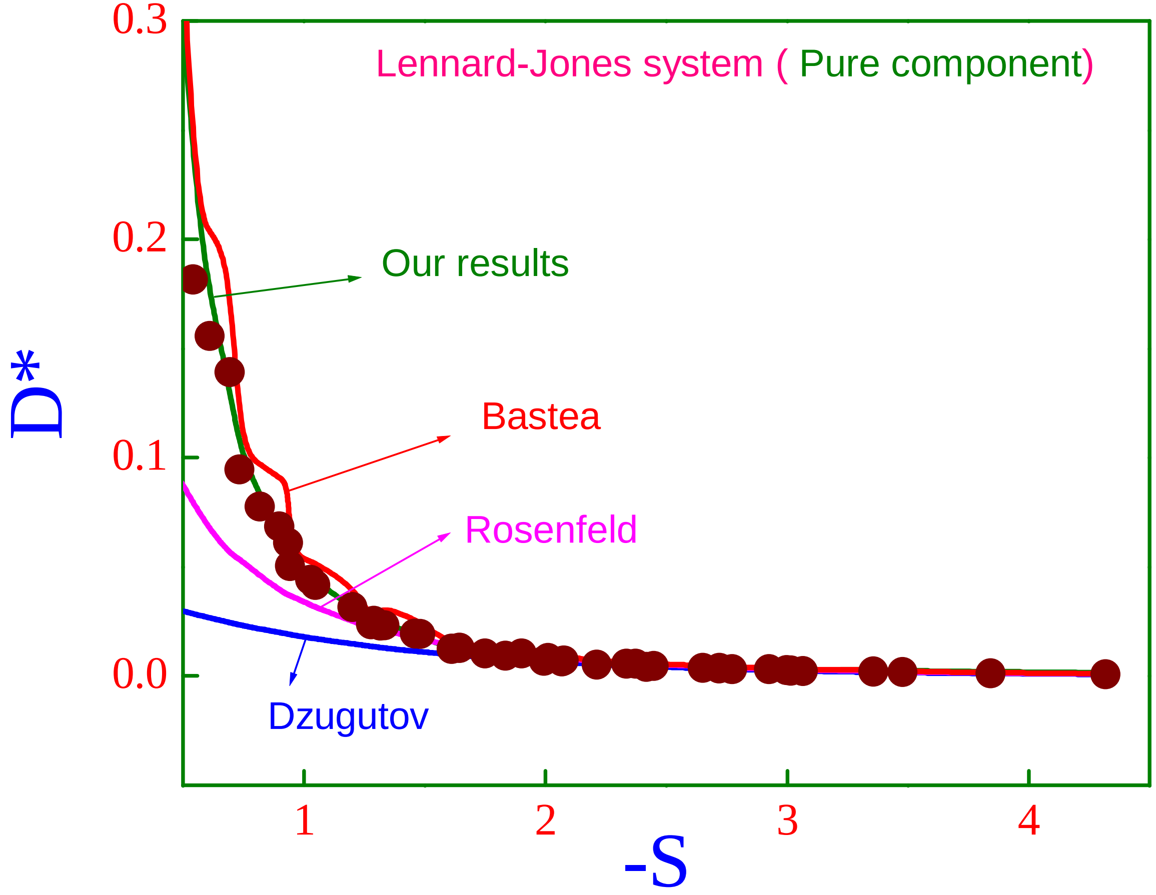
- Universal Scaling Laws of Diffusivity
- Scaled Diffusivity expressed in terms of excess entropy obtained from the Radial Distribution Function g(**r**), (essentially number density around a solute).



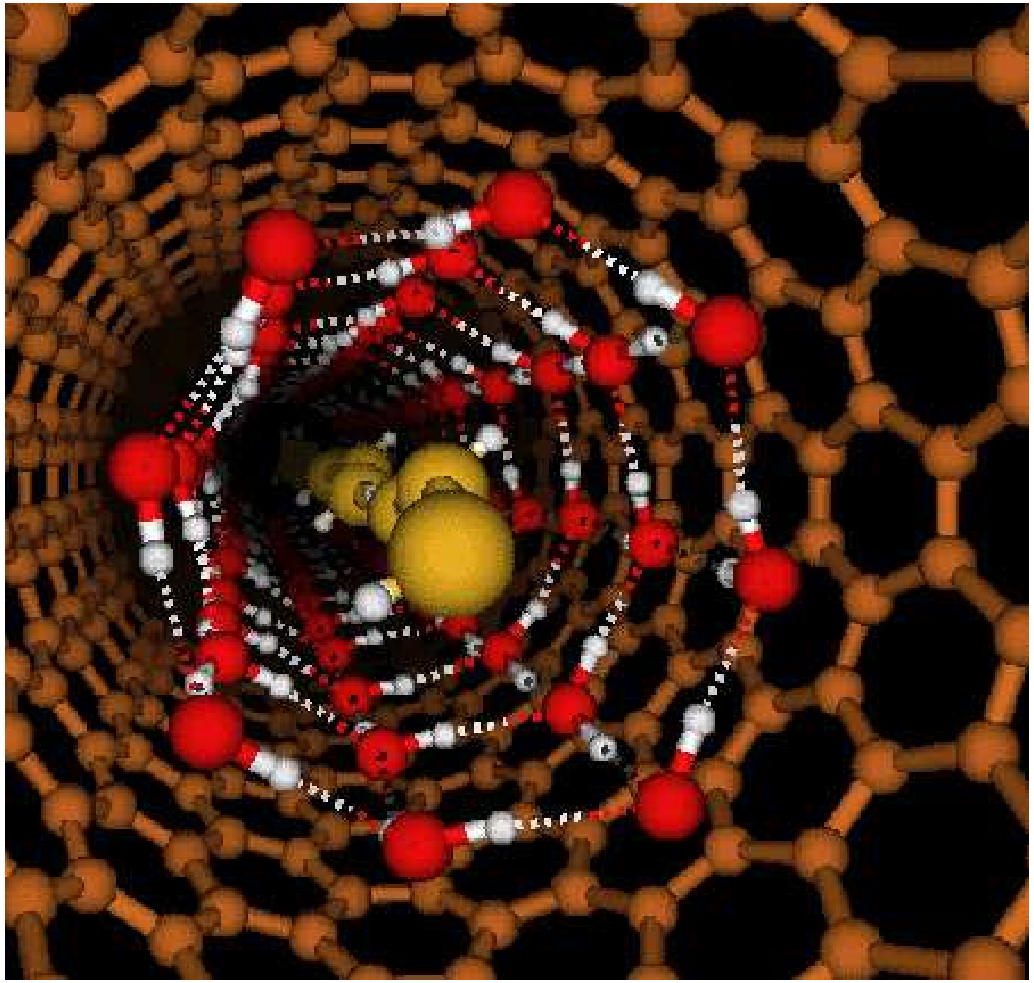
Universal Scaling Laws of Diffusivity derived for Fluid Mixtures by approximating the mode coupling theory expressions

Scaled Diffusivity: $D_\mu{}^* = A \exp[-S_\mu]$

Excess entropy: $S_\mu = \sum_\nu \rho_\nu \int d\mathbf{r}\, [\, g_{\mu\nu}(\mathbf{r}) \ln g_{\mu\nu}(\mathbf{r}) - (g_{\mu\nu}(\mathbf{r}) - 1)\,]$



A. Samanta, Sk. M. Ali, and S. K. Ghosh, Phys. Rev. Lett. 87, 245901 (2001), ; 92, 145901 (2004).



Nanotube Water

The water molecules into a carbon nanotube exist in the form of a "wire“, surrounded by another water structure, a cylindrical sheath of water. Neutron scattering along with computer Simulations.

Fluid-like behavior was observed at temperatures far below the freezing point of normal water.

The water chain allows a freer movement of protons along the chain.

This anomalous behavior might help to explain other phenomena featuring nm-scale confined water such as water migration from soil to plants via xylem vessels and the proton translocation in transmembrane proteins.

Colloids: A system of biological interest

Tunable interaction potential

DFT of inhomogeneous colloidal suspension

$$u(r_{12})=A\exp[-\kappa(r_{12}-d)]/r_{12}$$

$$\kappa^2=(4\pi\beta/\varepsilon)[\rho_0 Ze^2 + \Sigma\, \rho_\alpha Z_\alpha{}^2 e^2]$$

Tunable two-body interaction by changing ρ_0 and ρ_α

Colloidal dispersion in a planar slit/cylindrical pore

implication in blood flow through veins

flow through porous membranes

Phase ordering in charged colloids

PHYSICAL REVIEW E **VOLUME 57, NUMBER 2** **FEBRUARY 1998**

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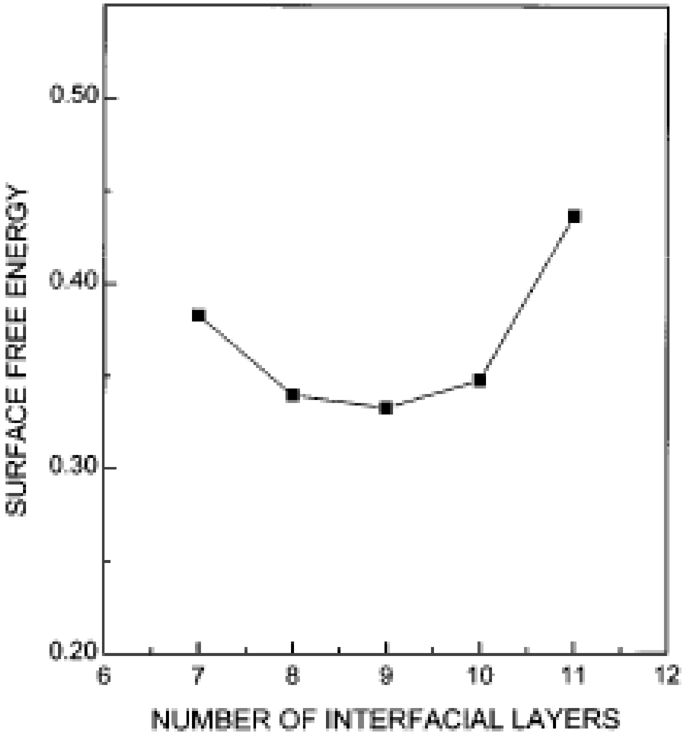


FIG. 1. Plot of calculated surface free energy vs number of interfacial layers for fcc liquid (111) interface of hard sphere fluid.

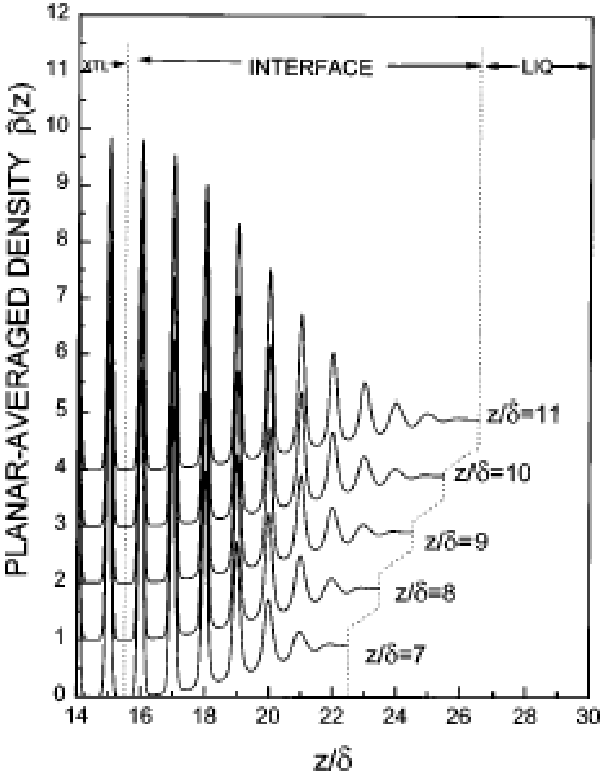


FIG. 2. Plot of planar averaged interfacial density profile $\hat{\rho}(z)$ for the (111) fcc liquid interface of hard sphere fluid for several values of interfacial width.

TABLE I. Layerwise weighted density, particle number, and contribution to excess free energy.

		Layer number										
Δz	quantity	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th
7	$\bar{\rho}_i$	0.5755	0.7458	0.8098	0.8456	0.9241	0.9280	0.9184				
	n_i	0.9381	0.9269	0.9067	0.8814	0.8562	0.8360	0.8236				
	$\psi_0 n_i$	1.8119	2.8112	3.2396	3.4510	4.1028	4.0464	3.8888				
8	$\bar{\rho}_i$	0.5674	0.7090	0.7684	0.8165	0.9193	0.9297	0.9191	0.9176			
	n_i	0.9377	0.9292	0.9133	0.8926	0.8702	0.8494	0.8334	0.8241			
	$\psi_0 n_i$	1.7708	2.5626	2.9355	3.2445	4.1180	4.1302	3.9425	3.8828			
9	$\bar{\rho}_i$	0.5614	0.6796	0.7330	0.7874	0.9085	0.9253	0.9173	0.9213	0.9166		
	n_i	0.9375	0.9307	0.9180	0.9008	0.8814	0.8618	0.8446	0.8317	0.8245		
	$\psi_0 n_i$	1.7407	2.2777	2.6939	3.0399	4.0566	4.1425	3.9766	3.9567	3.8748		
10	$\bar{\rho}_i$	0.5568	0.6563	0.7036	0.7598	0.8925	0.9150	0.9118	0.9255	0.9209	0.9154	
	n_i	0.9373	0.9318	0.9214	0.9071	0.8902	0.8725	0.8556	0.8412	0.8306	0.8247	
	$\psi_0 n_i$	1.7181	2.2392	2.5061	2.8517	3.9309	4.0831	3.9715	4.0456	3.9469	3.8637	
11	$\bar{\rho}_i$	0.5532	0.6379	0.6795	0.7346	0.8725	0.9000	0.9030	0.9277	0.9252	0.9178	0.9148
	n_i	0.9372	0.9327	0.9240	0.9118	0.8972	0.8813	0.8654	0.8508	0.8387	0.8296	0.8249
	$\psi_0 n_i$	1.7009	2.1340	2.3600	2.6868	3.7638	3.9678	3.9262	4.1149	4.0307	3.9115	3.8593

DYNAMICAL PHENOMENA

- Diffusion Phenomena in Complex Fluid Mixtures
- Flow through Nanopores
- Diffusion Assisted End-to-End Relaxation Dynamics of Polymer Chain
- Trapping of Diffusion Assisted System in External Periodic Field: Coherent Stochastic Resonance
- One-Dimensional Unified Description of Multi-Dimensional Dynamical Processes in Condensed Phase

Diffusion Phenomena

- Spontaneous: Thermal Fluctuation Driven
  - Concentration/chemical potential driven
- External Stimulus Driven: Response
  - Diffusion in the field of an external periodic force.
  - Coherent Stochastic Resonance:
    - Applications in separation technology (such as gel electrophoresis)

- Dimensionality dependence:
  - Bulk diffusion
  - Diffusion in Slits or Pores:
    - Single-File Diffusion: Diffusion is strictly one-dimensional
      - No particle can overtake each other.

Theories of Diffusivity:

- Mode Coupling Theory for bulk
- MCT coupled with weighted density functional theory for diffusion in pores
- Other aspects of diffusion

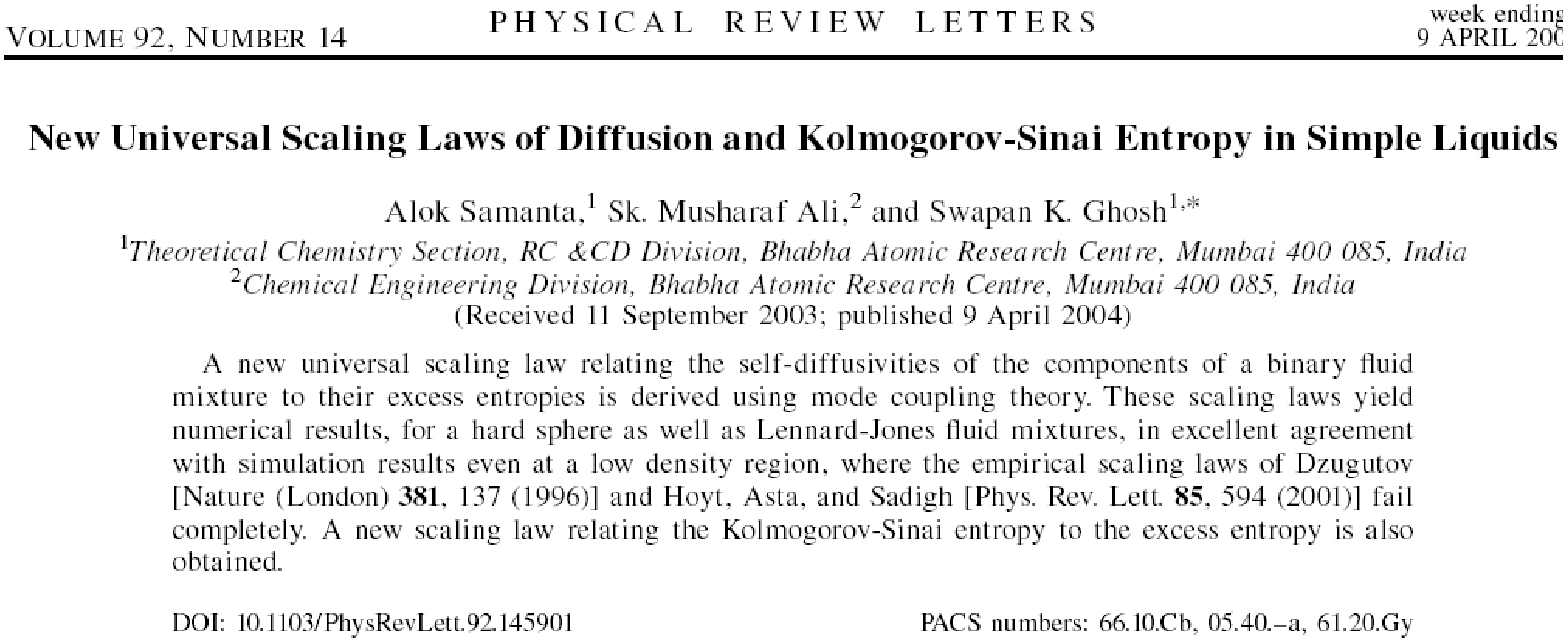
Diffusion in One-Dimension

- Seemingly simple text book material becomes complicated at least in two situations.
- When the diffusion (read noise) is further subjected to an external periodic force.
  - Leads to Coherent Stochastic Resonance and finds applications in separation technology (such as gel electrophoresis),
- When the diffusion is strictly one-dimensional such that no particle can overtake each other.
  - Known as **Single-File Diffusion** and is ubiquitous in nature (such as zeolites, carbon nanotubes and ion channels).

Dr Tusar Bandyopadhyay

Dr Alok Samanta

Dr Shashwati Roy



VOLUME 92, NUMBER 14 PHYSICAL REVIEW LETTERS week ending 9 APRIL 200

New Universal Scaling Laws of Diffusion and Kolmogorov-Sinai Entropy in Simple Liquids

Alok Samanta,[1] Sk. Musharaf Ali,[2] and Swapan K. Ghosh[1,*]
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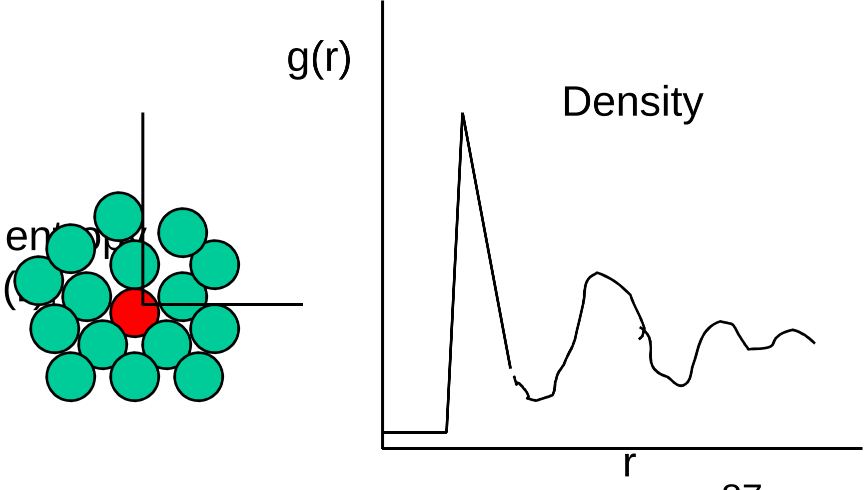
•Relationship between the transport coefficients and structural properties has remained as one of the most challenging and non-trivial tasks in the
field of condensed phase dynamics.

•Universal Scaling Laws of Diffusivity

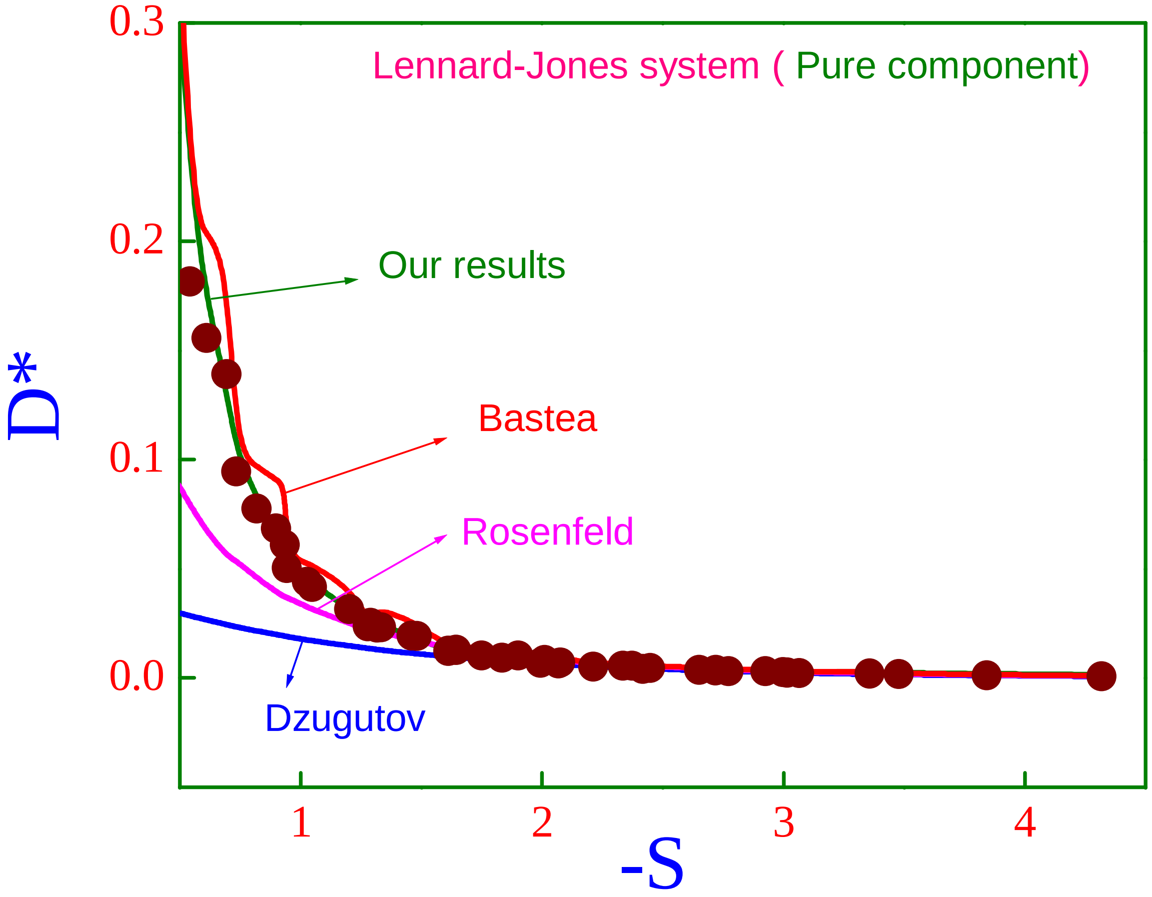
•Scaled Diffusivity expressed in terms of excess entropy
obtained from the Radial Distribution Function g(r)
(essentially number density around a solute).



Universal Scaling Laws of Diffusivity derived for Fluid Mixtures by approximating the mode coupling theory expressions

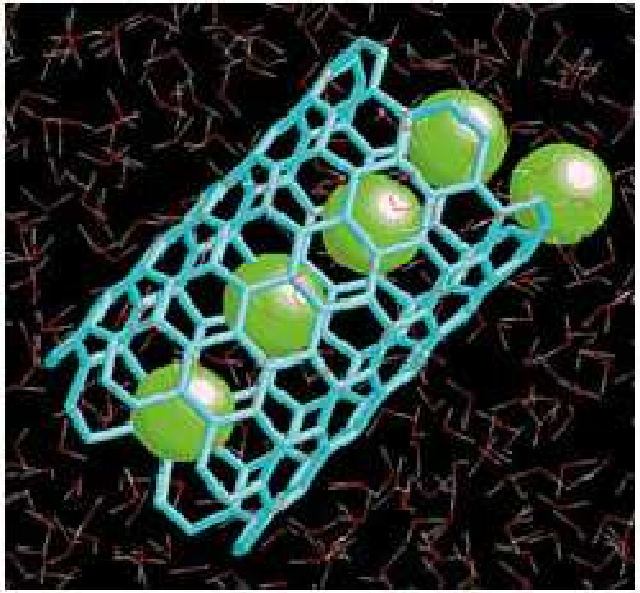
Scaled Diffusivity: $D_\mu{}^* = A \exp[-S_\mu]$

Excess entropy: $S_\mu = \sum_\nu \rho_\nu \int d\mathbf{r}\, [\, g_{\mu\nu}(\mathbf{r}) \ln g_{\mu\nu}(\mathbf{r}) - (g_{\mu\nu}(\mathbf{r}) - 1)\,]$



A. Samanta, Sk. M. Ali, and S. K. Ghosh, Phys. Rev. Lett. 87, 245901 (2001), ; 92, 145901 (2004).

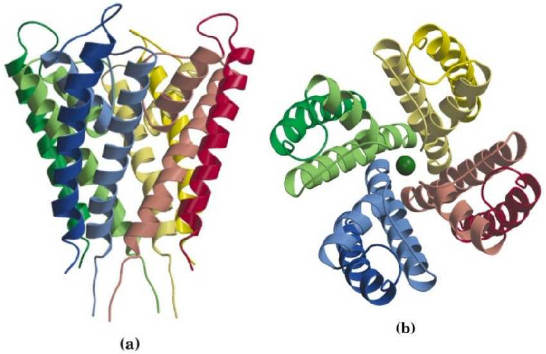
Diffusion in Nanopores

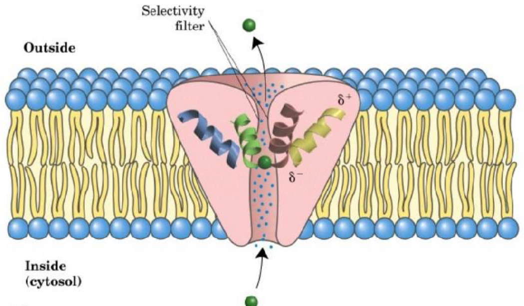


Single-File

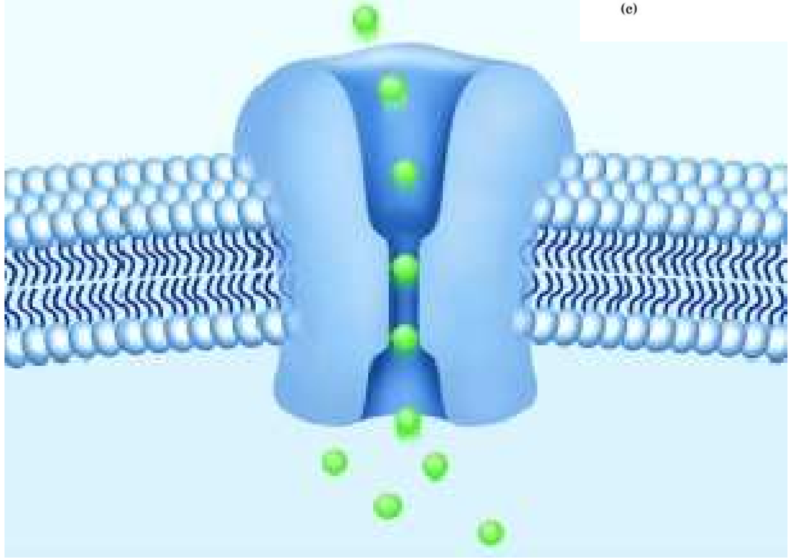
Diffusion

K+ ion Channel



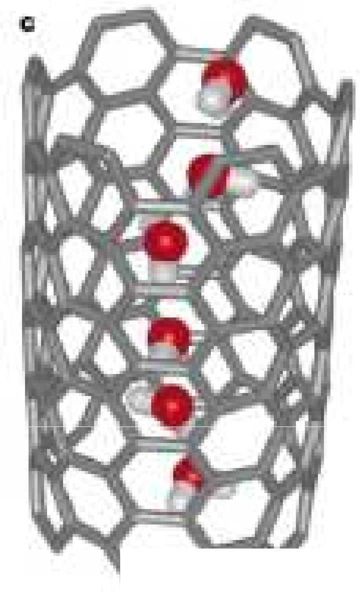


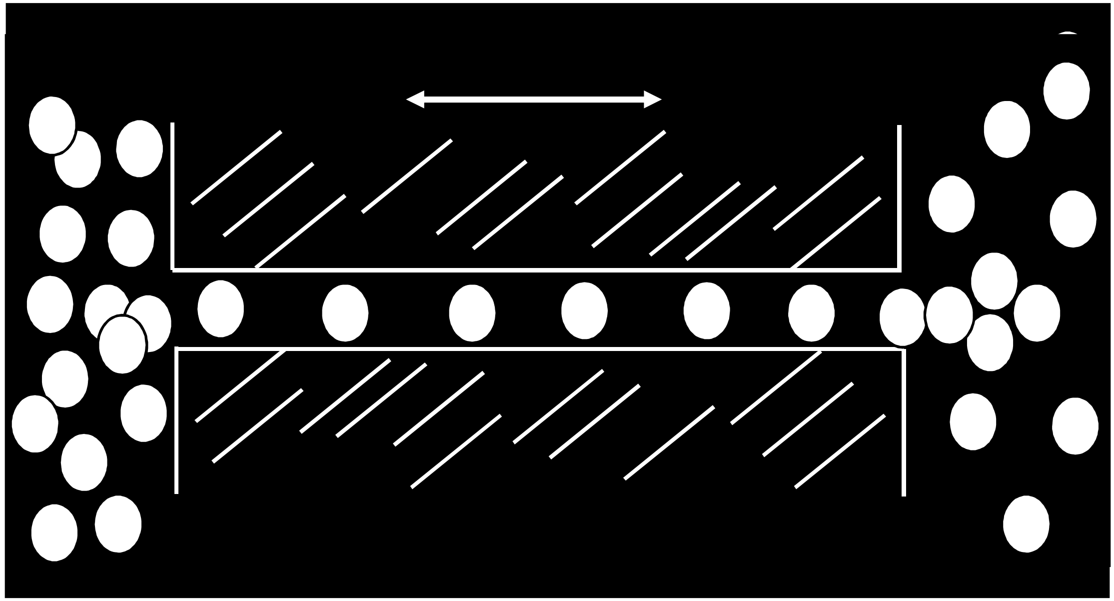
(c)



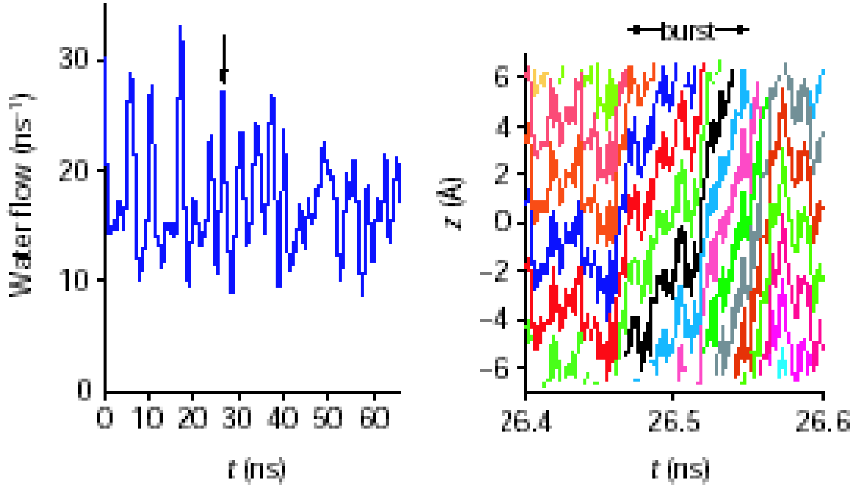
Single-File conduction through smooth channel

Objective: To study the translocation dynamics of particles in a finite and smooth single-file channel connected with reservoirs at the ends: dependence on channel length and inter-particle interaction.





Water loses 2 of 4 H-bonds; yet it hydrates the C-nanotube



Rupturing the water chain is energetically involves energy cost - intermittent flow

THE JOURNAL OF CHEMICAL PHYSICS **125**, 201103 (2006)

Bursts in single-file motion mediated conduction

Shashwati Roy Majumder,[a] Tusar Bandyopadhyay,[b] and Swapan K. Ghosh[c]
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(Received 15 September 2006; accepted 30 October 2006; published online 28 November 2006)

THE JOURNAL OF CHEMICAL PHYSICS **127**, 054706 (2007)

Enhanced flow in smooth single-file channel

Shashwati Roy Majumder,[a] Niharendu Choudhury,[b] and Swapan K. Ghosh[c]
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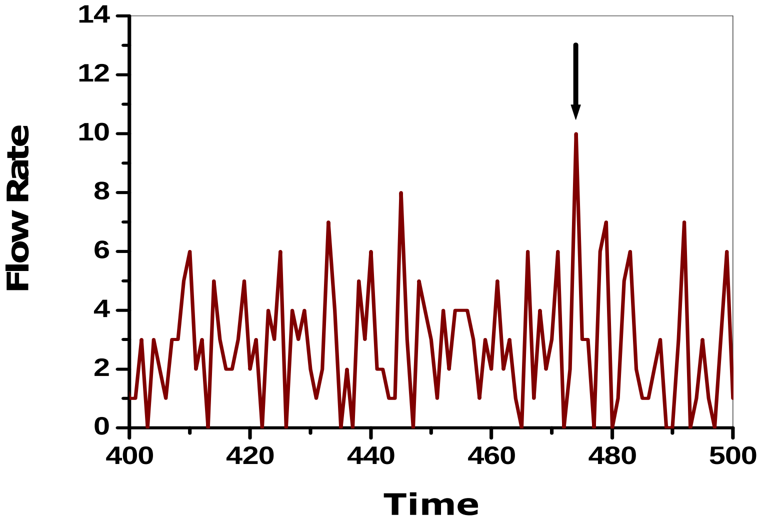
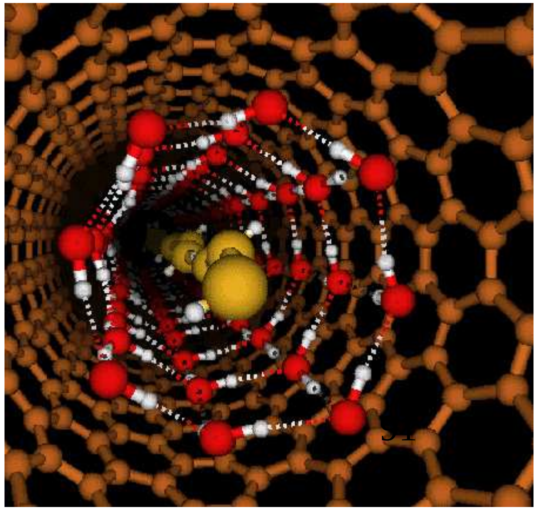
Mumbai 400 085, India

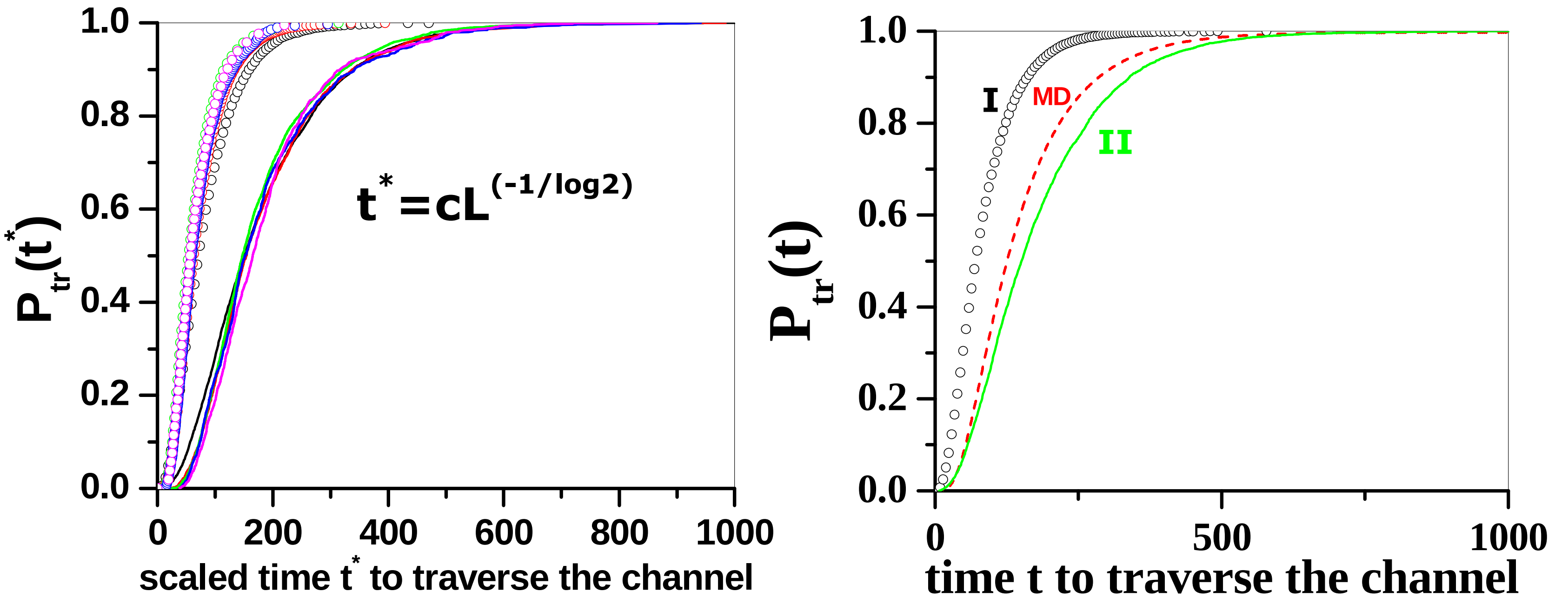
(Received 16 March 2007; accepted 2 July 2007; published online 7 August 2007)



Conduction Bursts- Universal Feature of SFM



$$P_{tr}(t)\ (\text{or, } P_r(t)) = \frac{\text{No. of translocated (or returned) particles within spent time t}}{\text{Total No. of translocated (or returned) partcls within } 10^5 \text{ CA steps}}$$



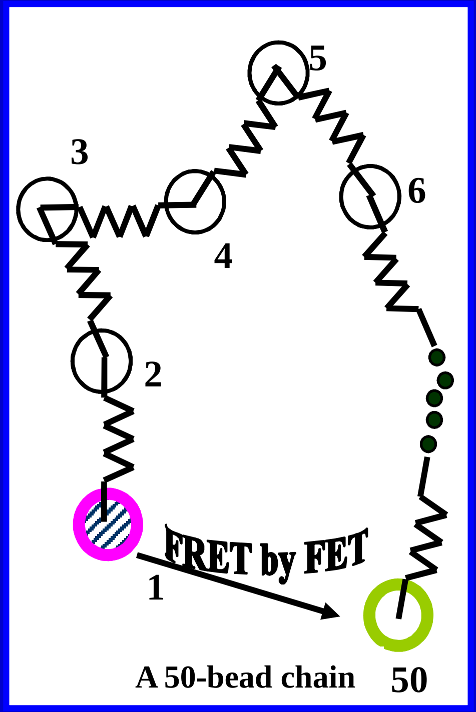
Cumulative translocation probabilities for different channel lengths show universality as a function of scaled time t*.

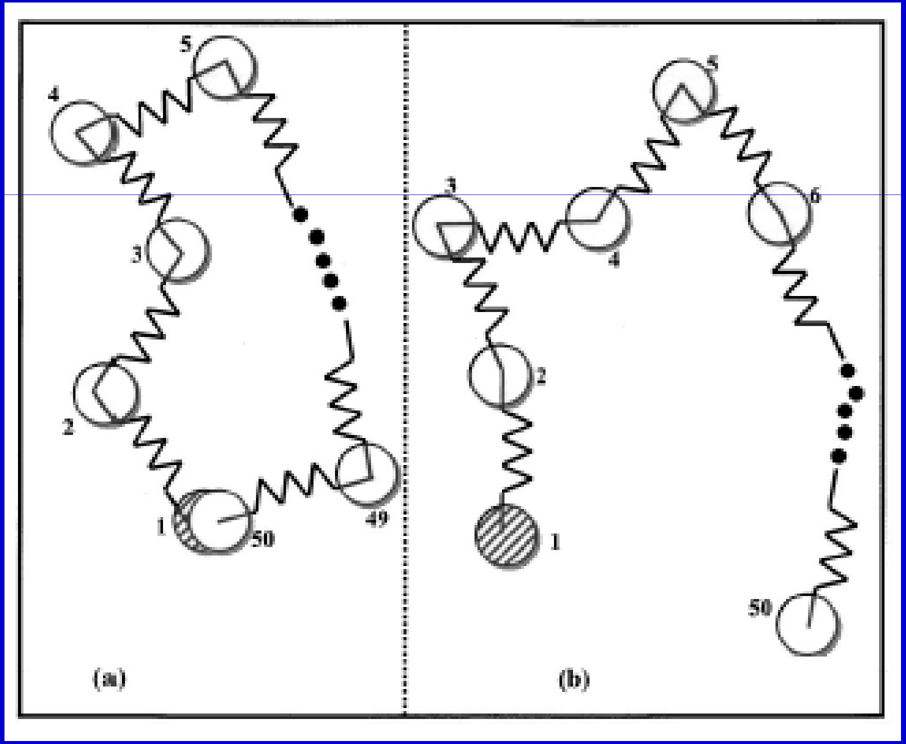
- With proper scaling of time curves for different inter-particle interaction also shows universal behavior.

JOURNAL OF CHEMICAL PHYSICS VOLUME 119, NUMBER 1 1 JULY 2003

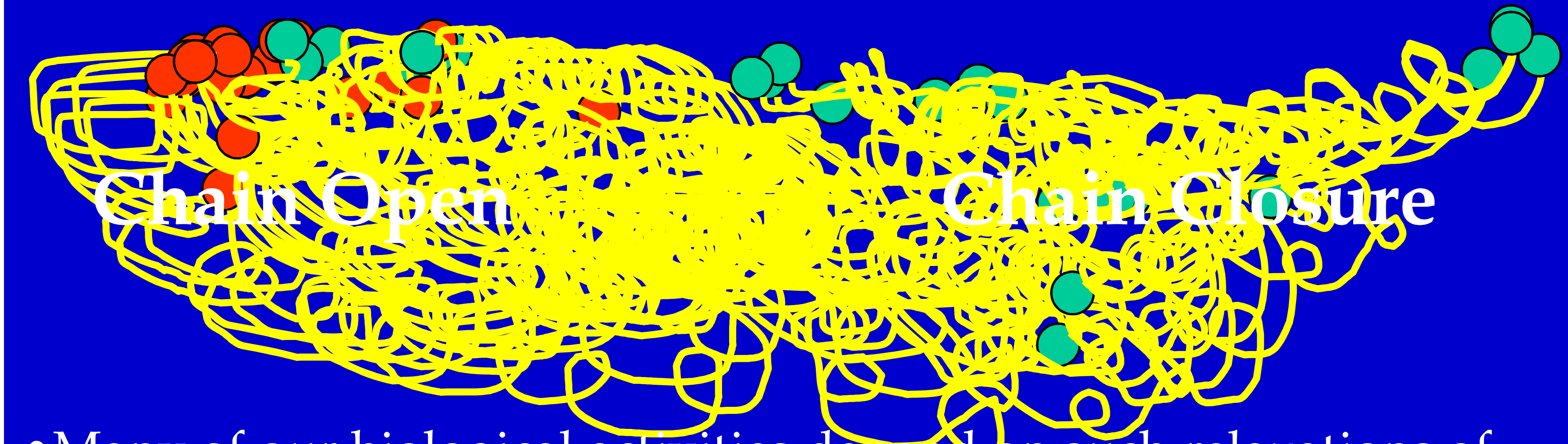
Diffusion assisted end–to–end relaxation of a flexible Rouse polymer chain: Fluorescence quenching through a model energy transfer

Tusar Bandyopadhyay[a] and Swapan K. Ghosh[b]
Theoretical Chemistry Section, Radiation Chemistry and Chemical Dynamics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India





End-to-end relaxation of polymer (protein) chain



- Many of our biological activities depend on such relaxations of proteins and biopolymers

- **The problem :** How to distinguish between a closure and opening transitions, traditionally monitored by time-dependent fluorescence resonance energy transfer (FRET) signal

- **The Solution:** Theories have been developed utilizing Zwanzig's treatment of irreversible thermodynamics to address this issue. Criteria for a definitive signature of closure Transition have been formulated.

The result will have significant impact in the field of protein folding dynamics

Why to study such systems?

- Conformational transitions in bioploymers and proteins
- Many specific biological activities depends on the folding characteristics of the concerned chain molecules
- Statistical mechanics of the flexible chain molecules, left alone, is rich enough that calls for an attention

How to study such systems?

- Experimentally via fluorescence resonance energy transfer (FRET) between the chromohores attached to the selective locations along the chain backbone
- Theoretically we propose a recipe in order to obtain FRET signals, for such a system, based on Zwanzig's generalization of Irreversible Thermodynamics

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) = \underset{\uparrow}{\hat{L}}\rho(\mathbf{r},t) + \int_0^t dt'\, \underset{\uparrow}{M}(t')\hat{L}\rho(\mathbf{r},t-t') \underset{\uparrow}{-} k(\mathbf{r})\rho(\mathbf{r},t)$$

With or without Conformational Tr.

Memory term

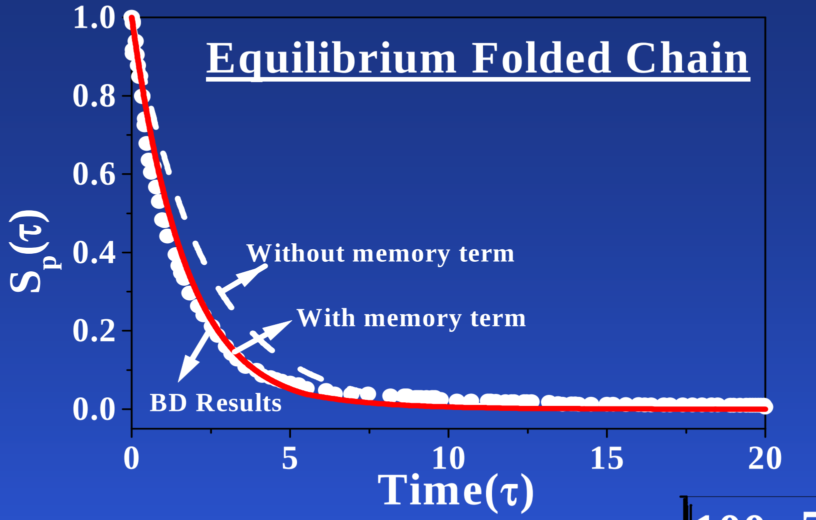
FET

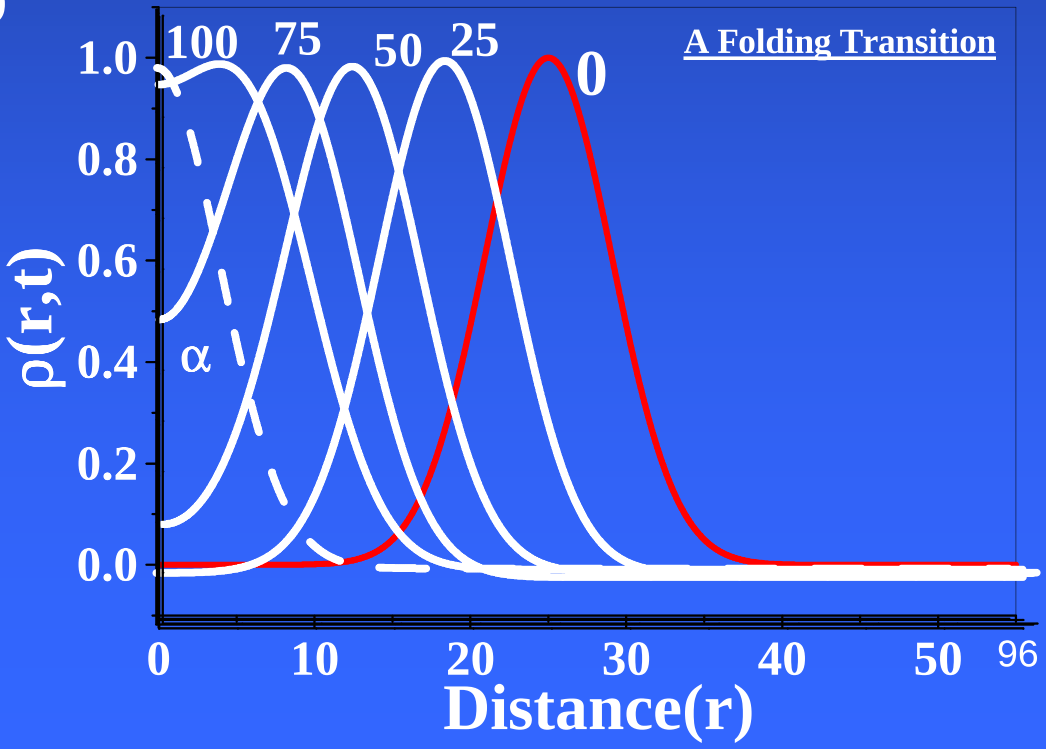
$$S_p(t) = \int d\mathbf{r}\,\rho(\mathbf{r},t)$$

FRET Signal

↔

Typical Results





Effect of electric field on the diffusion-influenced escape probabilities of ion-pair systems.

Coherent Stochastic Resonance:

The phenomena that the diffusion-driven particle mobility towards a trap increases in the presence of an externally applied driving field and attains a maximum at a particular resonant frequency of the field.

Applications:

Electrophoretic separation of proteins, DNA, the chromatographic and the recently proposed elegant model of high performance chromatographic separation, tuned by modulated external fields, of chemical species from a mixture with close properties.

J. Chem. Phys. **104** (23), 15 June 1996 0021-9606/96/104(23)/9563/6/$10.00 © 1996 American Institute of Physics 9563

Colloidal dispersion confined in a planar slit: A density functional approach

Niharendu Choudhury and Swapan K. Ghosh
Heavy Water Division, Bhabha Atomic Research Centre, Bombay 400085, India

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JOURNAL OF CHEMICAL PHYSICS VOLUME 111, NUMBER 4 22 JULY 1999

Colloidal suspensions in charged cylindrical pores: A perturbative density functional approach

Niharendu Choudhury and Swapan K. Ghosh
Theoretical Chemistry Section, RC & CD Division, Chemistr
Bombay 400 085, India

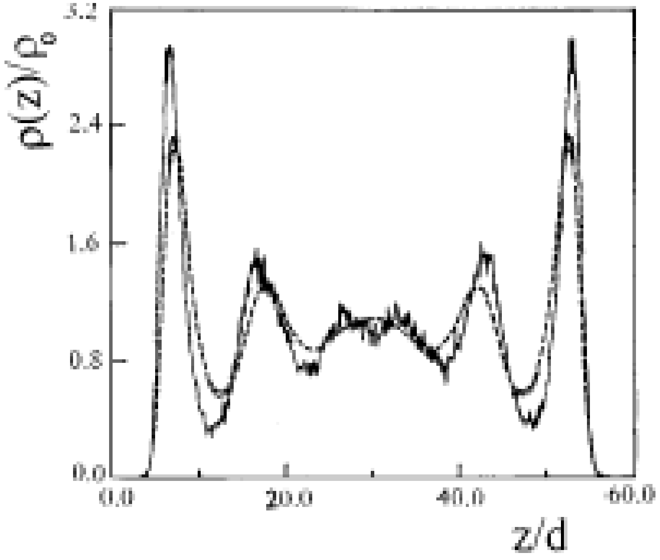
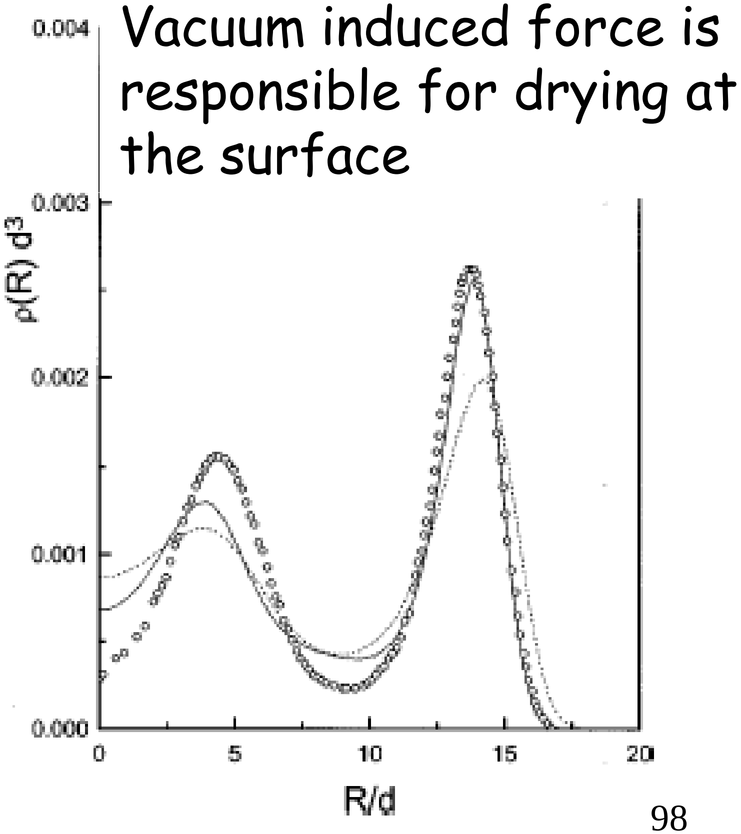


FIG. 3. Plot of the density profile $\rho(z)/\rho_0$ vs z/d for a model colloidal suspension for wall separation of 60d. The parameters and the key are same as in Fig. 1.



Vacuum induced force is responsible for drying at the surface

PHYSICAL REVIEW E **67**, 061113 (2003)

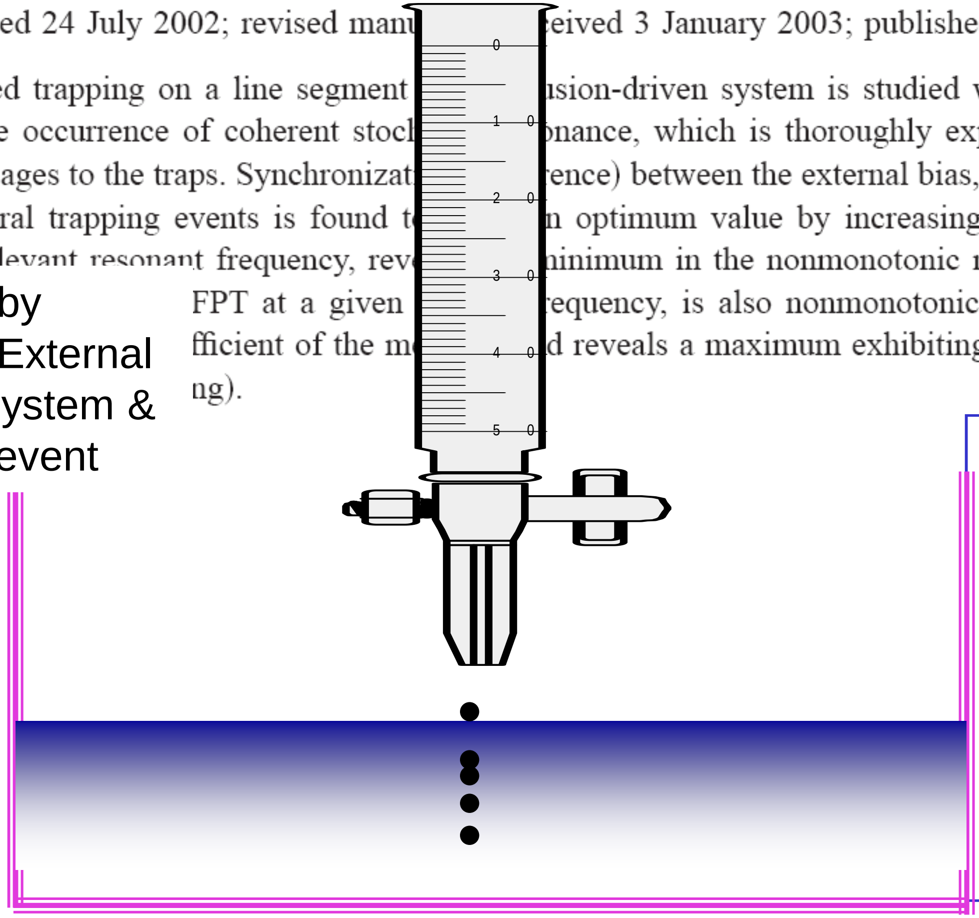
Coherent and incoherent trapping of a diffusion-assisted system in the presence of an external periodic field

Tusar Bandyopadhyay* and Swapan K. Ghosh†
Theoretical Chemistry Section, Radiation Chemistry and Chemical Dynamics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

(Received 24 July 2002; revised manu eived 3 January 2003; published 23 June 2003)

Field induced trapping on a line segment usion-driven system is studied with an aim to gain an insight into the occurrence of coherent stoc nance, which is thoroughly explored as synchronized mean-free passages to the traps. Synchronizat ence) between the external bias, the noise in the system and the temporal trapping events is found t n optimum value by increasing the forcing frequency towards the relevant resonant frequency, rev inimum in the nonmonotonic mean-free-passage time FPT at a given equency, is also nonmonotonic when considered as a fficient of the m d reveals a maximum exhibiting the least synchroniza- ng).

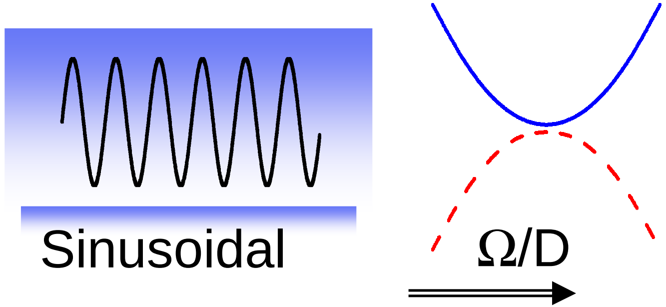
Separation of ions by synchronization of External field, Noise in the system & Temporal trapping event



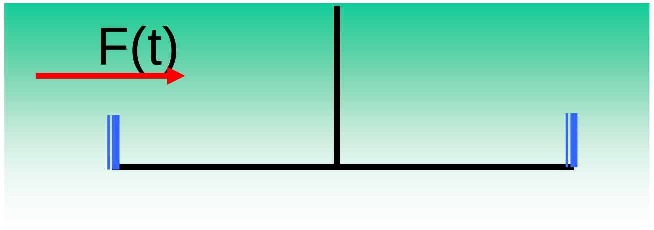
Electric Field

- Coherent/Incoherent trapping at line boundaries is characterized & the counterintuitive constructive facet of noise behind the coherent trapping mechanism is explored

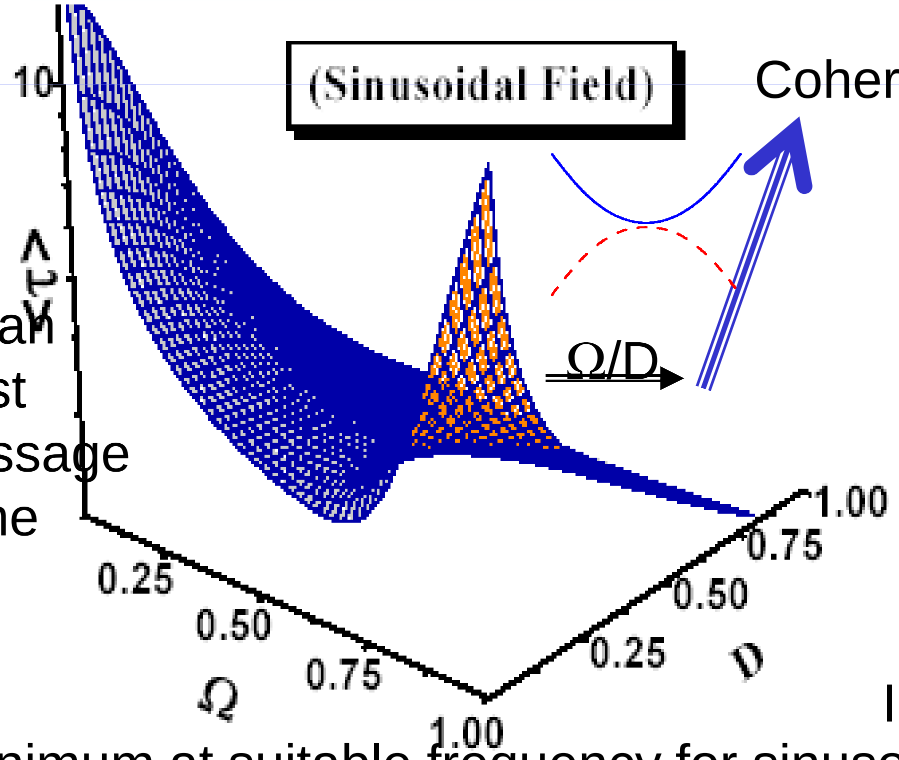
Electric Field assisted
trapping at
line boundaries



Coherent Stochastic Resonance: Interplay of Noise & Signal

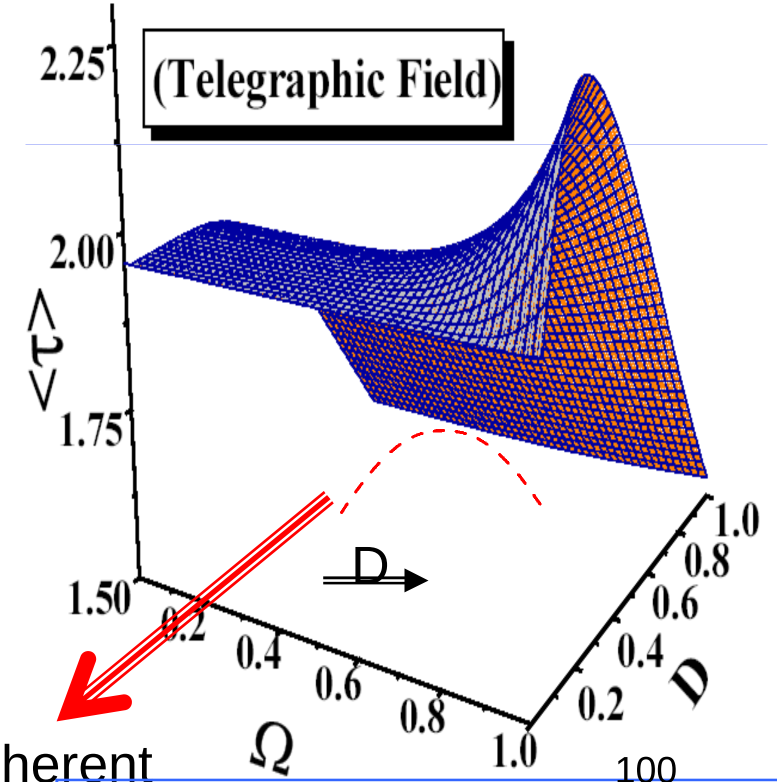


$$\frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2} - A F(\Omega t)\frac{\partial \rho}{\partial x}$$



Coherent

Mean
First
Passage
Time



Incoherent

Minimum at suitable frequency for sinusoidal field

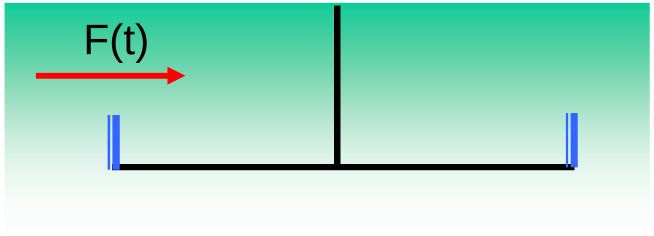
Phys. Rev. E 67, 061113 (2003)

PHYSICAL REVIEW E **67**, 061113 (2003)

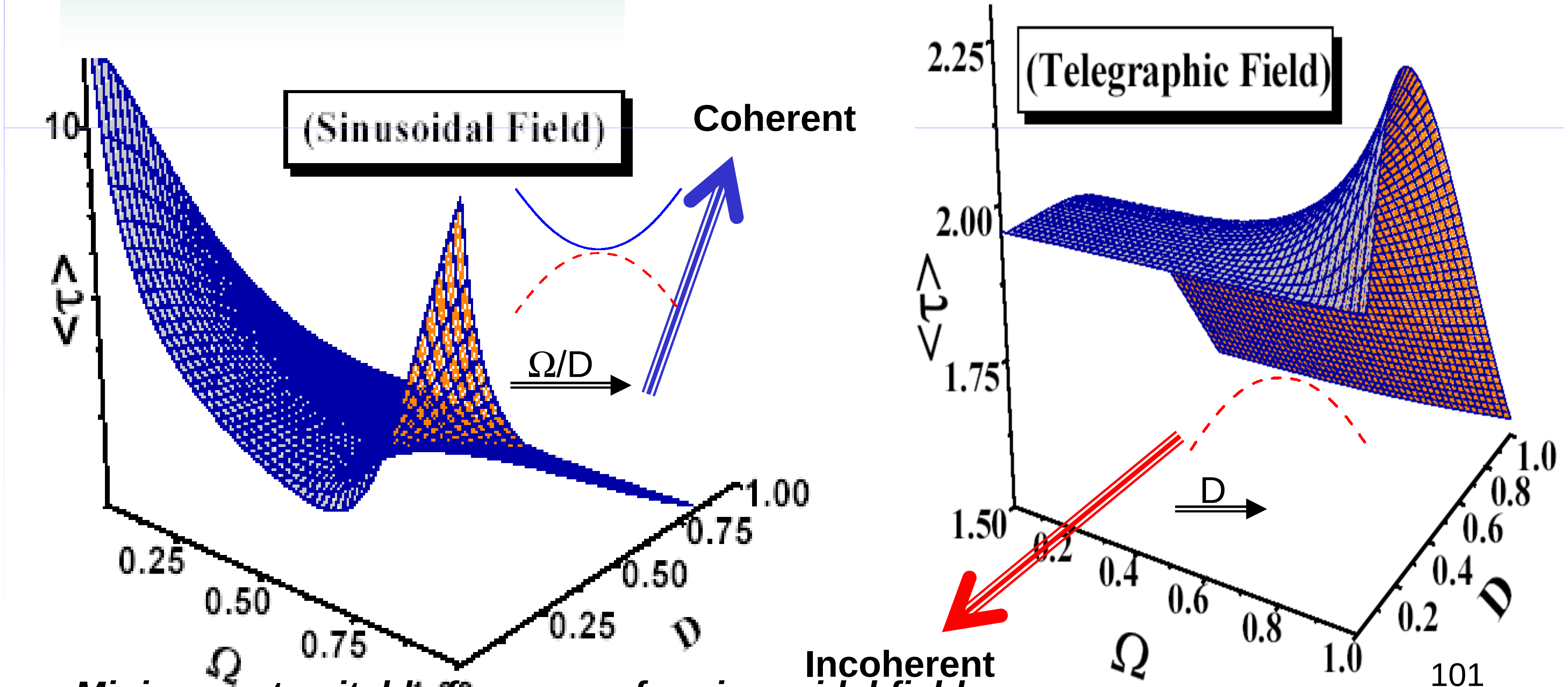
Coherent and incoherent trapping of a diffusion-assisted system in the presence of an external periodic field

Tusar Bandyopadhyay* and Swapan K. Ghosh†

Electric Field assisted trapping at line boundaries



$$\frac{\partial \rho}{\partial t} = D\,\frac{\partial^2 \rho}{\partial x^2} - A\,F(\Omega t)\,\frac{\partial \rho}{\partial x}$$



Minimum at suitable frequency for sinusoidal field

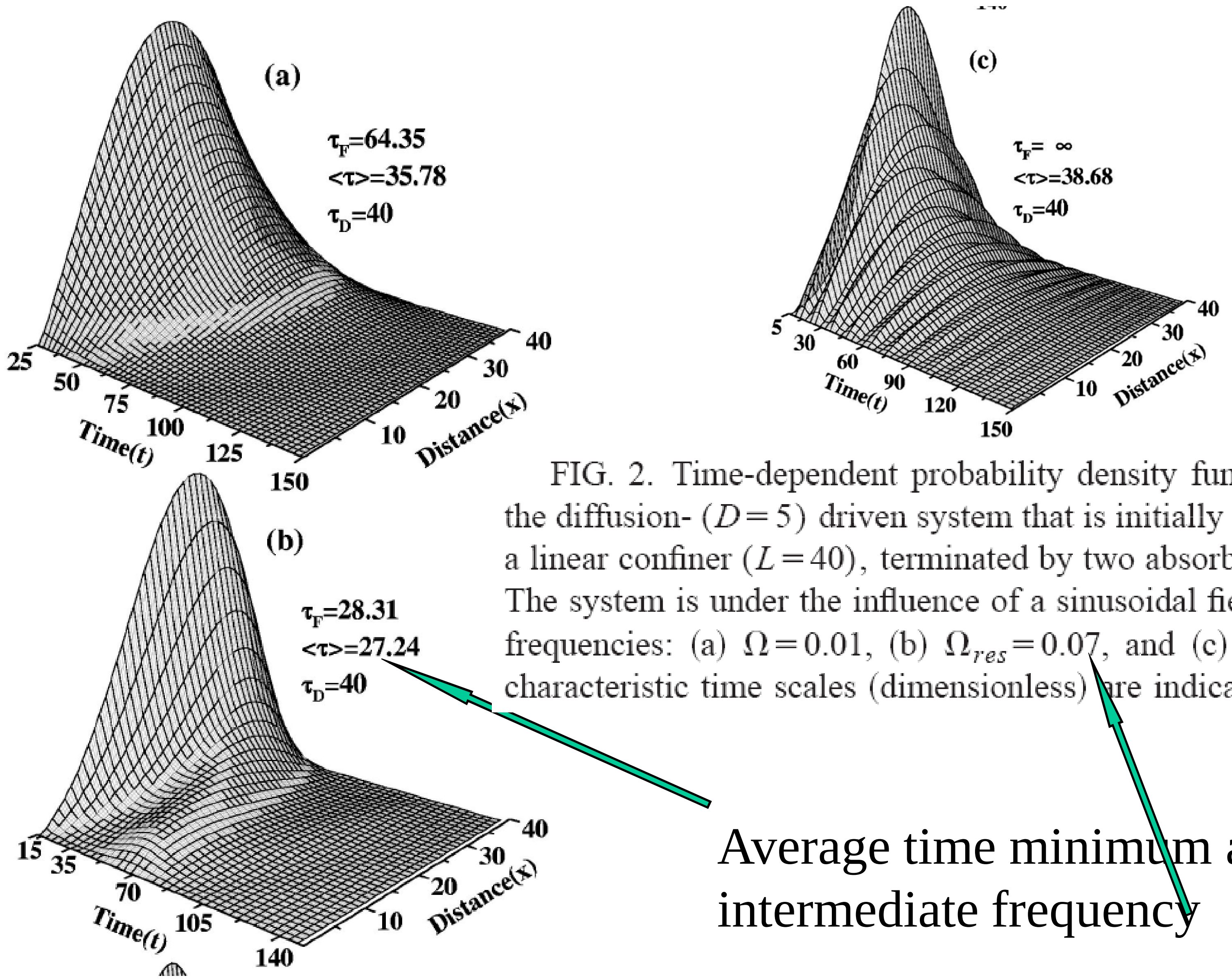


FIG. 2. Time-dependent probability density function $\rho(x,t)$ of the diffusion- $(D=5)$ driven system that is initially at the middle of a linear confiner $(L=40)$, terminated by two absorbing boundaries. The system is under the influence of a sinusoidal field with forcing frequencies: (a) $\Omega=0.01$, (b) $\Omega_{res}=0.07$, and (c) $\Omega=0.5$. Three characteristic time scales (dimensionless) are indicated.

Average time minimum at intermediate frequency

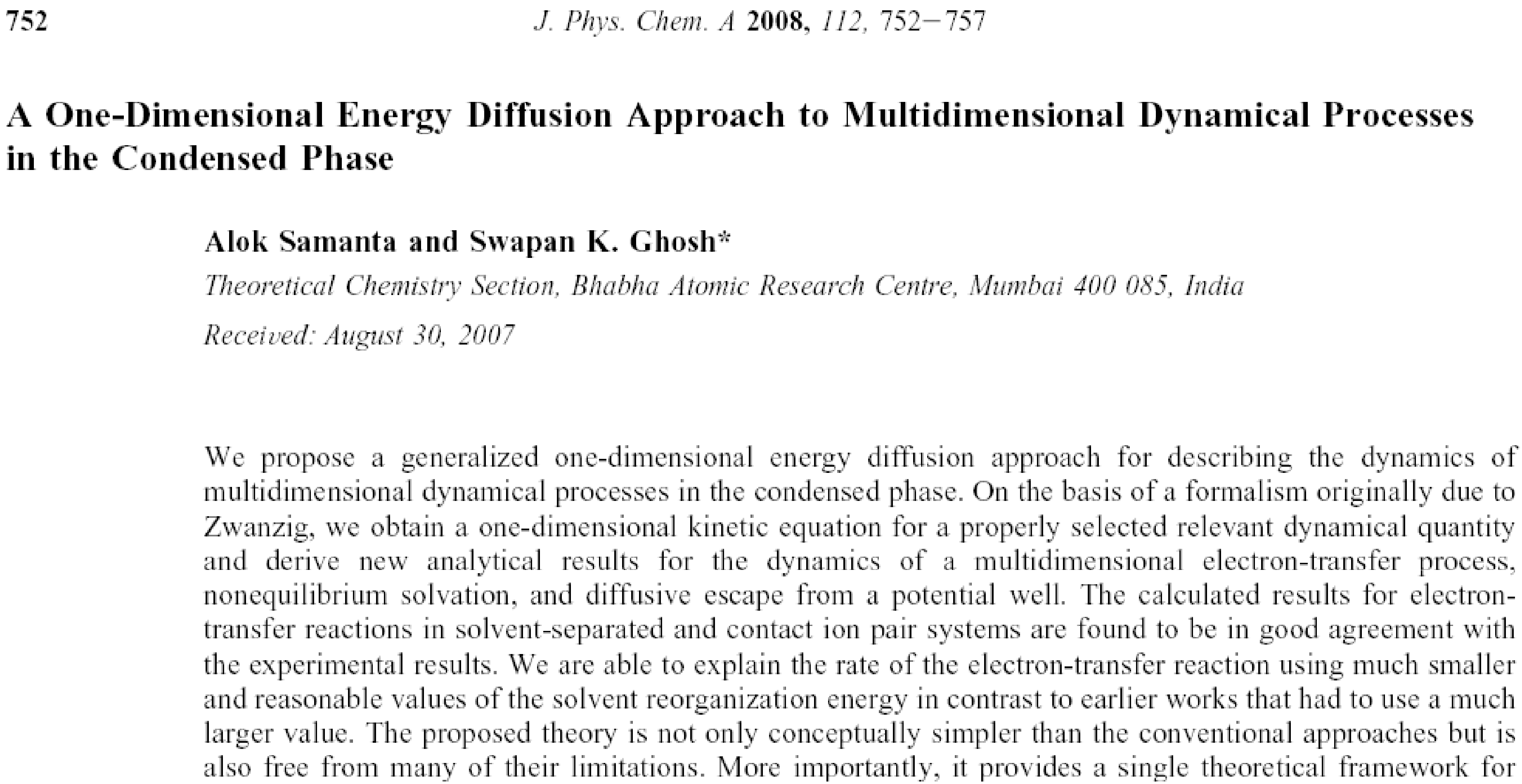
A Unified One-dimensional Energy Diffusion approach to Multidimensional Dynamical Process in Condensed Phase

Probability distribution of a suitable quantity $\rho(\gamma,t)$:

- A single unified theoretical framework for describing a wide variety of dynamical phenomena

- Bypassing the bottlenecks of the conventional approaches.

- This conceptually simple and computationally economic one-dimensional description of the multi-dimensional processes employs similar dynamical equations for different problems.



752 *J. Phys. Chem. A* **2008,** *112,* 752−757

A One-Dimensional Energy Diffusion Approach to Multidimensional Dynamical Processes in the Condensed Phase

Alok Samanta and Swapan K. Ghosh*

Theoretical Chemistry Section, Bhabha Atomic Research Centre, Mumbai 400 085, India

Received: August 30, 2007

We propose a generalized one-dimensional energy diffusion approach for describing the dynamics of multidimensional dynamical processes in the condensed phase. On the basis of a formalism originally due to Zwanzig, we obtain a one-dimensional kinetic equation for a properly selected relevant dynamical quantity and derive new analytical results for the dynamics of a multidimensional electron-transfer process, nonequilibrium solvation, and diffusive escape from a potential well. The calculated results for electron-transfer reactions in solvent-separated and contact ion pair systems are found to be in good agreement with the experimental results. We are able to explain the rate of the electron-transfer reaction using much smaller and reasonable values of the solvent reorganization energy in contrast to earlier works that had to use a much larger value. The proposed theory is not only conceptually simpler than the conventional approaches but is also free from many of their limitations. More importantly, it provides a single theoretical framework for

So far, the density has referred to electron density, particle number density, probability density for the end to end distance of polymer etc.

Now we consider the probability distribution P(γ,t) denoting the probability of any microscopic phase-space variable A (in general multi-dimensional) constrained to have a value γ.

Thus, one can have a probability P(E,t) for a system to have energy E at time t and have an energy diffusion equation and consider the one-dimensional dynamics.

Theoretical Formalism

The basic approach is based on an identification of a proper reaction coordinate (dynamical variable), obtaining a kinetic equation for the probability distribution of a microscopic phase-space variable A (multi-dimensional) constrained to have a value γ.

Distribution in γ space: $P(\gamma,t) = < \delta(A(t)-\gamma)>_{NE}$

One-dimensional generalised kinetic equation in γ-space

$$\partial P(\gamma,t)/\partial t = \partial/\partial\gamma\{\int_0^t d\tau\, D(\gamma,t-\tau)\, [\partial P(\gamma,t-\tau)/\partial\gamma +$$

$$\partial/\partial\gamma\{\beta V_{eff}(\gamma)\}\, P(\gamma,t-\tau)]\}$$

where time as well as γ-dependent diffusivity is defined as

$$D(\gamma,t)=<(dA(t)/dt)(dA/dt)|_{t=0}\, \delta(A(t)-\gamma)>/<\delta(A(t)-\gamma)>$$

and

effective Potential is: $\beta V_{eff}(\gamma) = -\ln<\delta(A-\gamma)>$

The Journal of Physical Chemistry Letters

Thermodynamics: From Cluster to Bulk

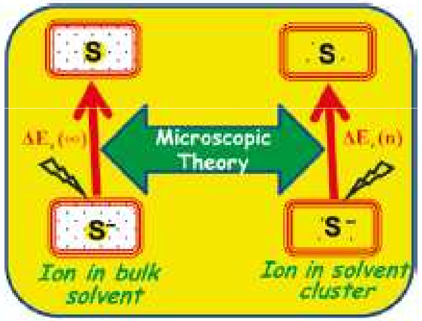
pubs.acs.org/JPCL

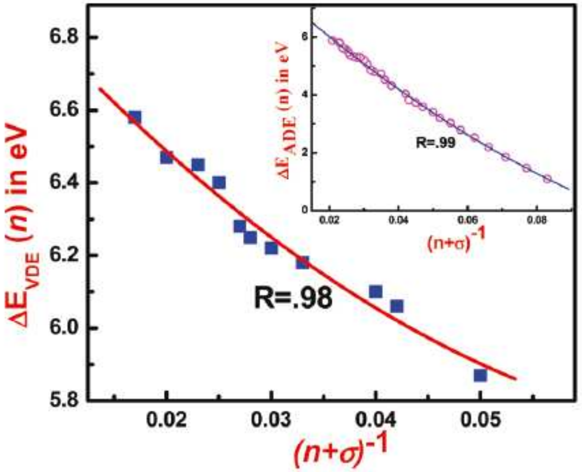
Generalized Microscopic Theory for the Detachment Energy of Solvated Negatively Charged Ions in Finite Size Clusters: A Step toward Bulk

A. K. Pathak, A. K. Samanta,* D. K. Maity,* T. Mukherjee, and S. K. Ghosh

Chemistry Group, Bhabha Atomic Research Centre, Mumbai-400085, India

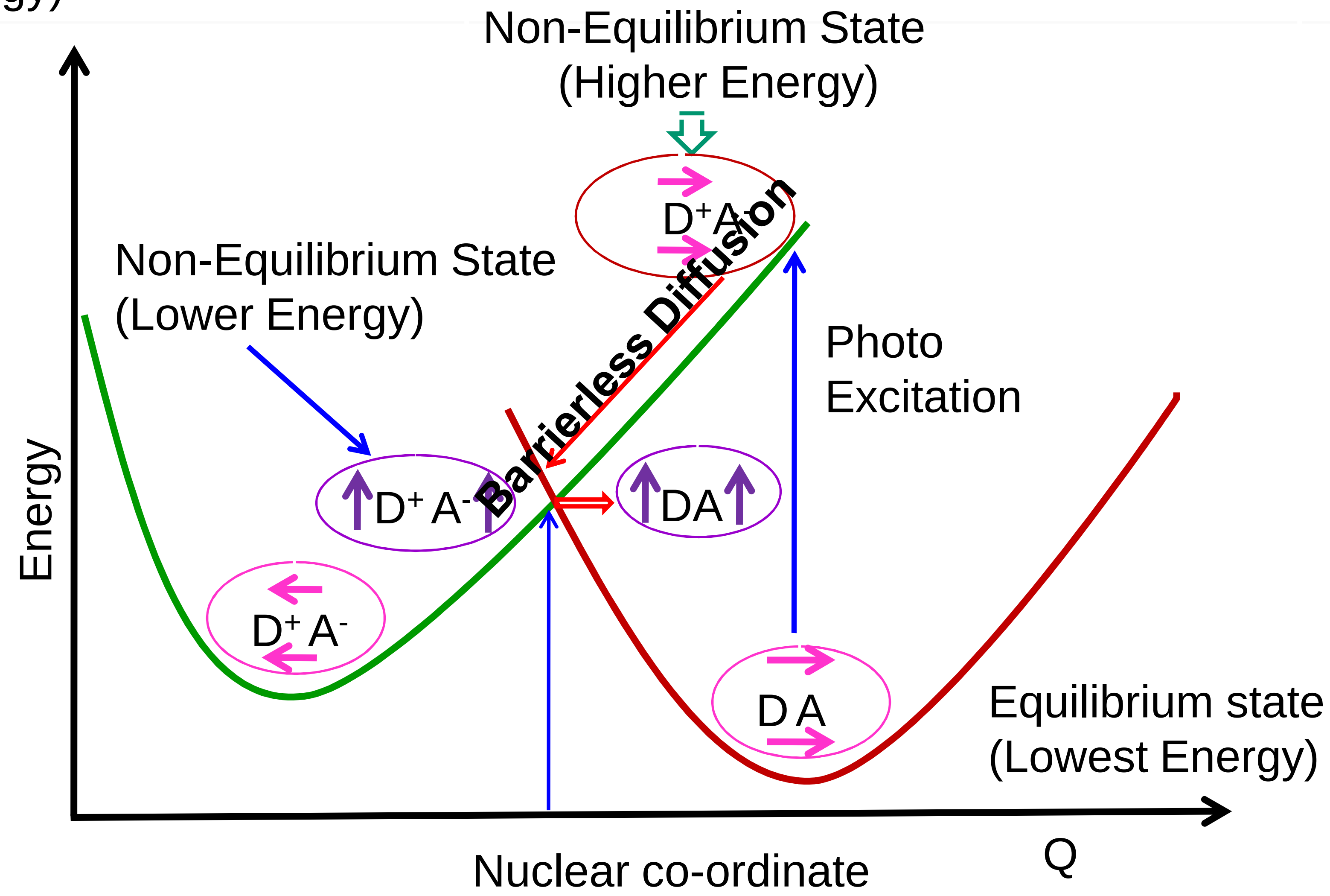
ABSTRACT A new general relation is derived for the size-dependent detachment energy of solvated negatively charged ions in finite size clusters based on a microscopic theory for systems with unknown interaction potentials. The relation is tested over a large number of different kinds of finite-size hydrated clusters of the type $A^{q-}(H_2O)_n$ (for spherical and nonspherical, singly and multiply charged ion A^{q-}), and an excellent agreement with experimental results is observed. More importantly, the robust scheme is shown to provide a route to obtain the bulk (infinite-size clusters) detachment energy from the results of finite-size clusters. Again, an excellent agreement with the experimental results is observed where the earlier models are shown to fail.





$$\Delta E_\nu(n) = \Delta E_\nu(\infty) + \frac{A_\nu}{n+\sigma} + \frac{B_\nu}{(n+\sigma)^2}$$

Barrierless Diffusion (BD): BD of photo excited non-equilibrium state (higher energy) to Non-equilibrium transition state ($Q^{\#}$) state (lower energy)



Non-Equilibrium State (Higher Energy)

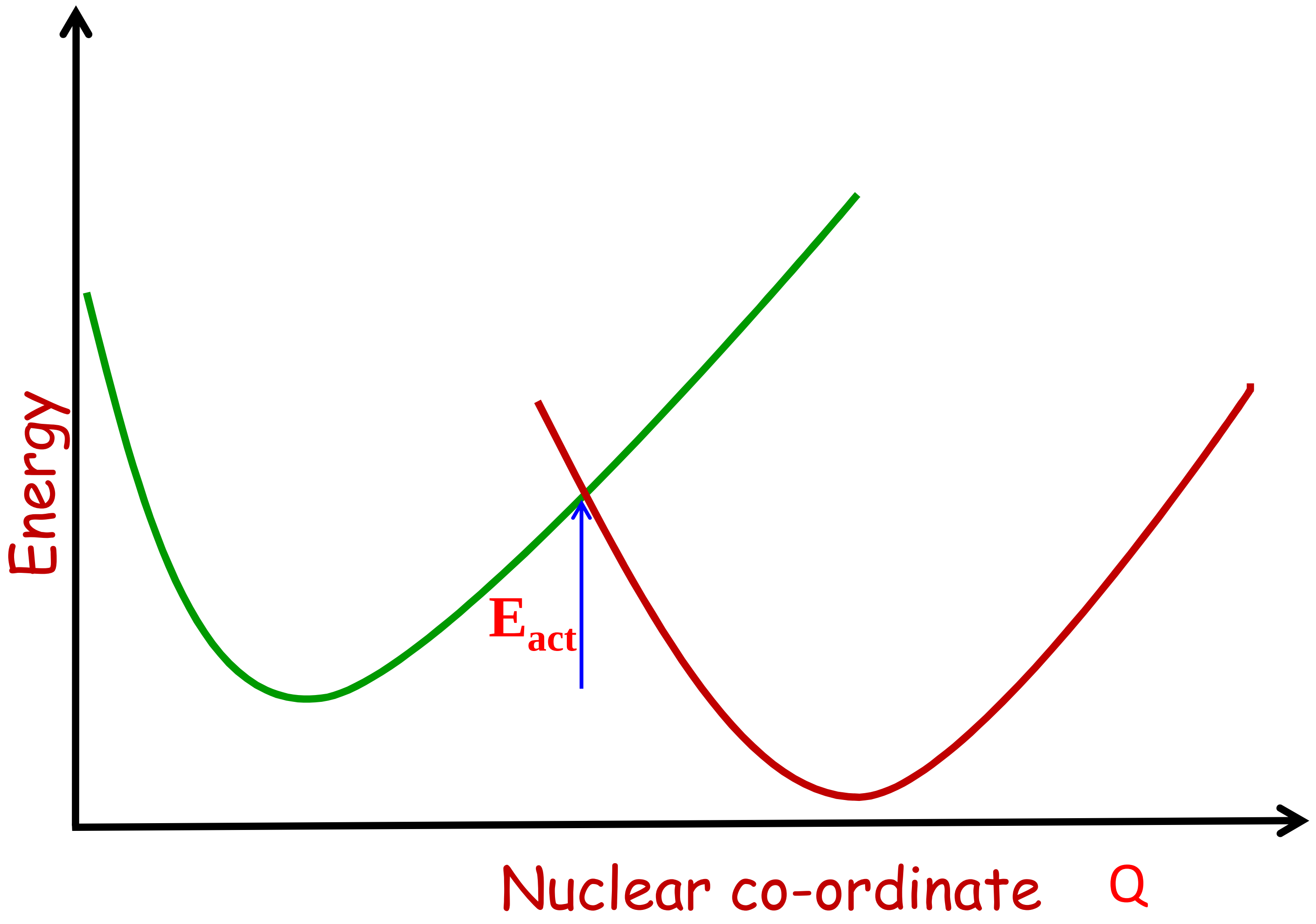
Non-Equilibrium State (Lower Energy)

Photo Excitation

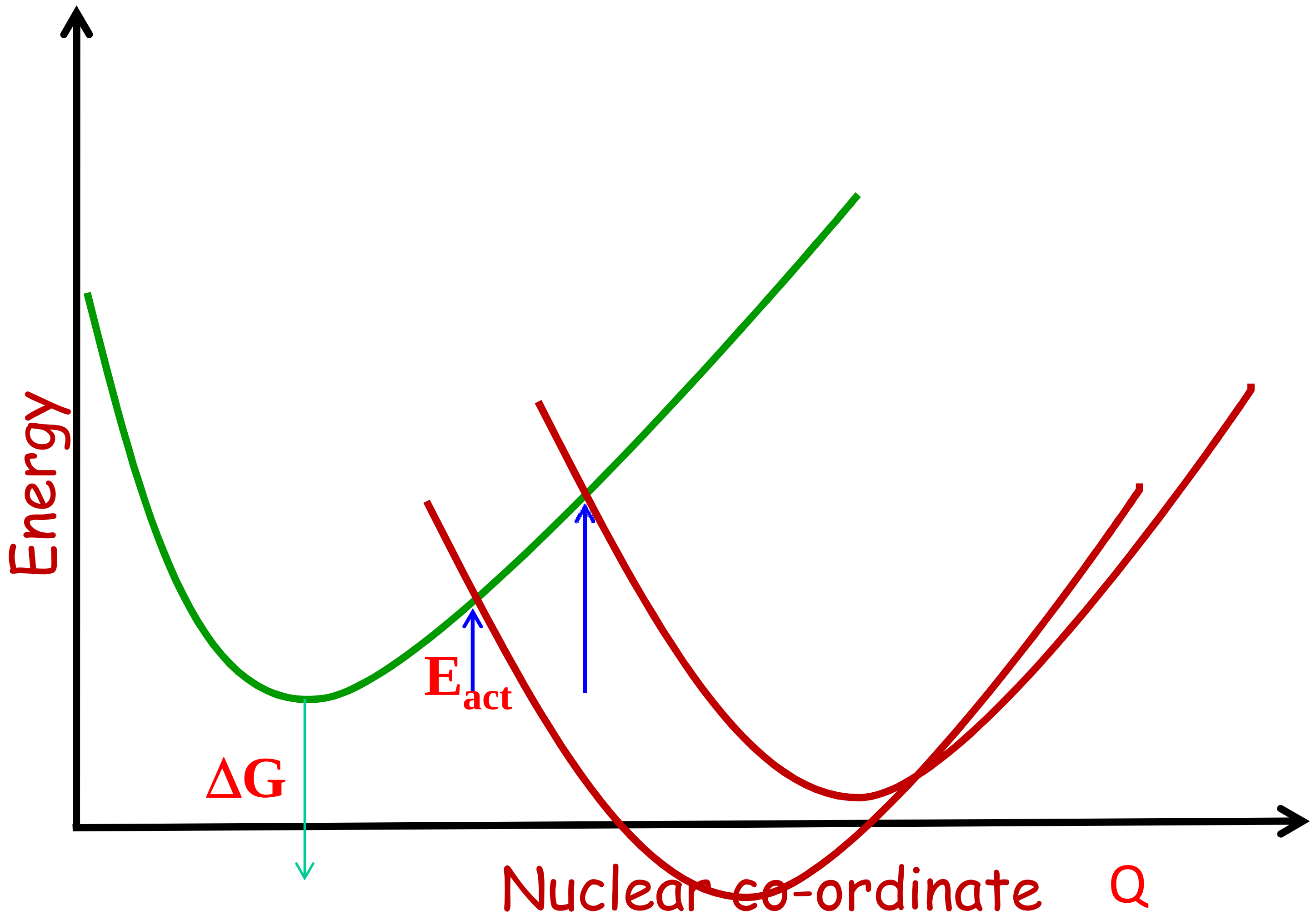
Equilibrium state (Lowest Energy)

Nuclear co-ordinate

Inverted Region



Inverted Region



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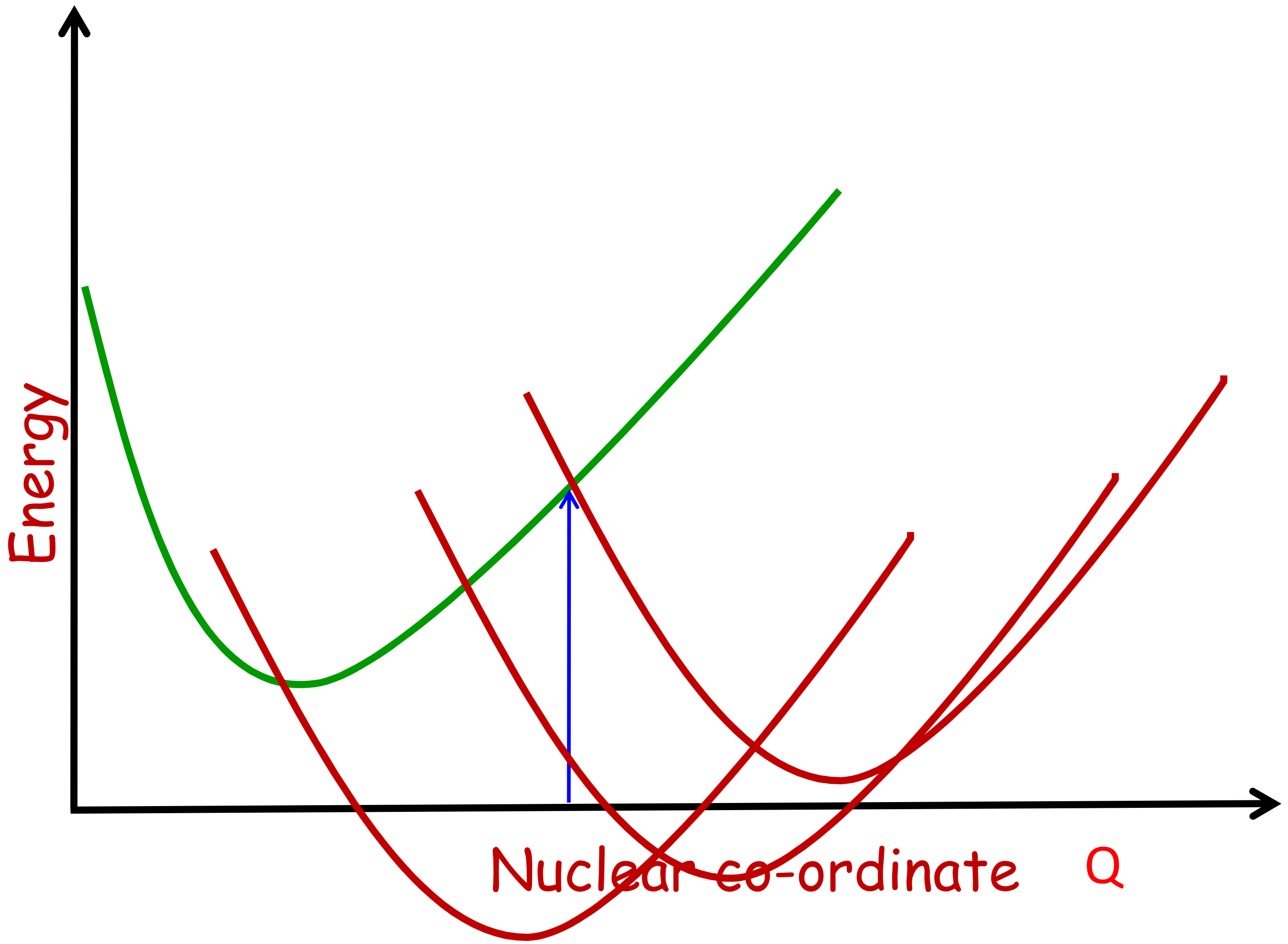
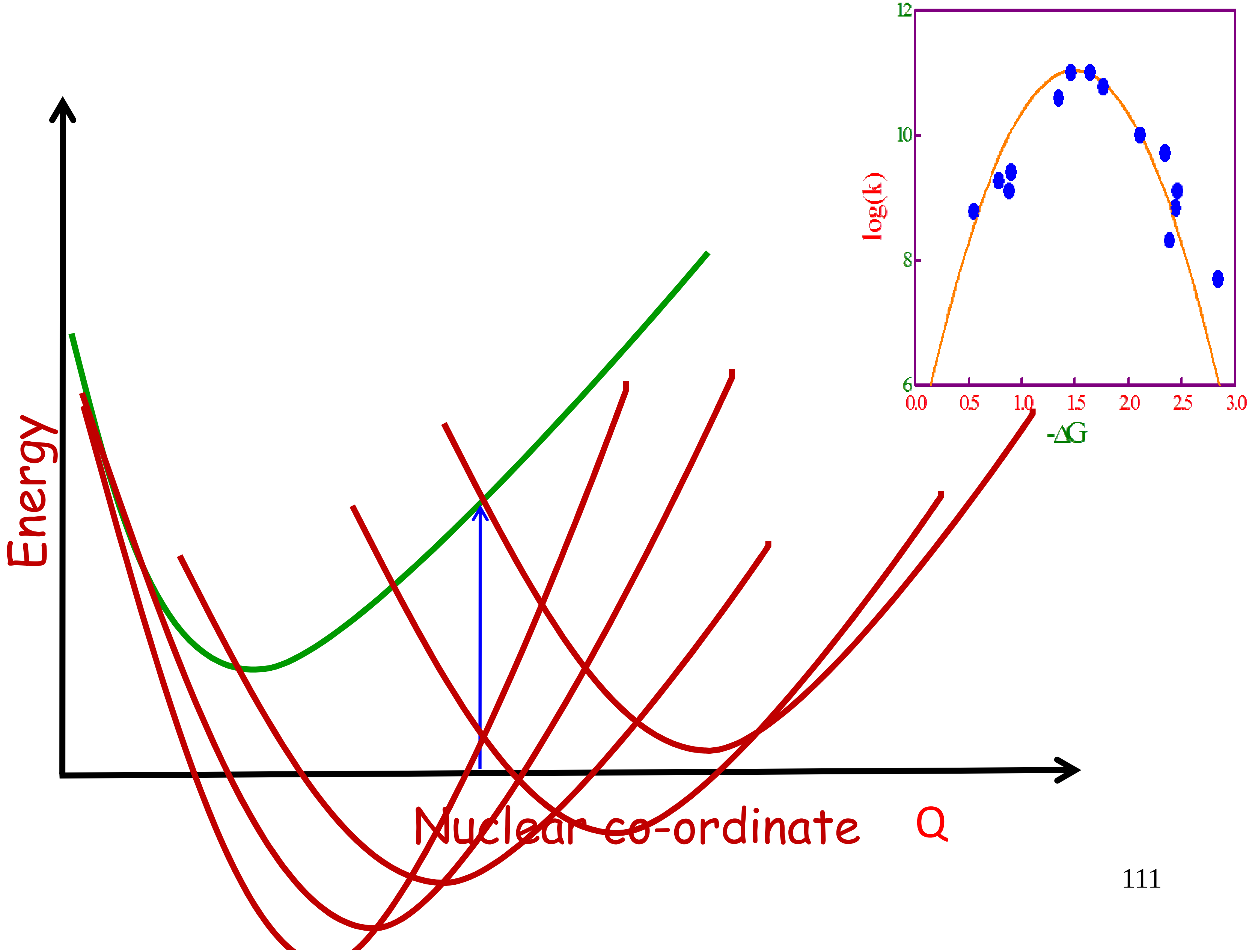
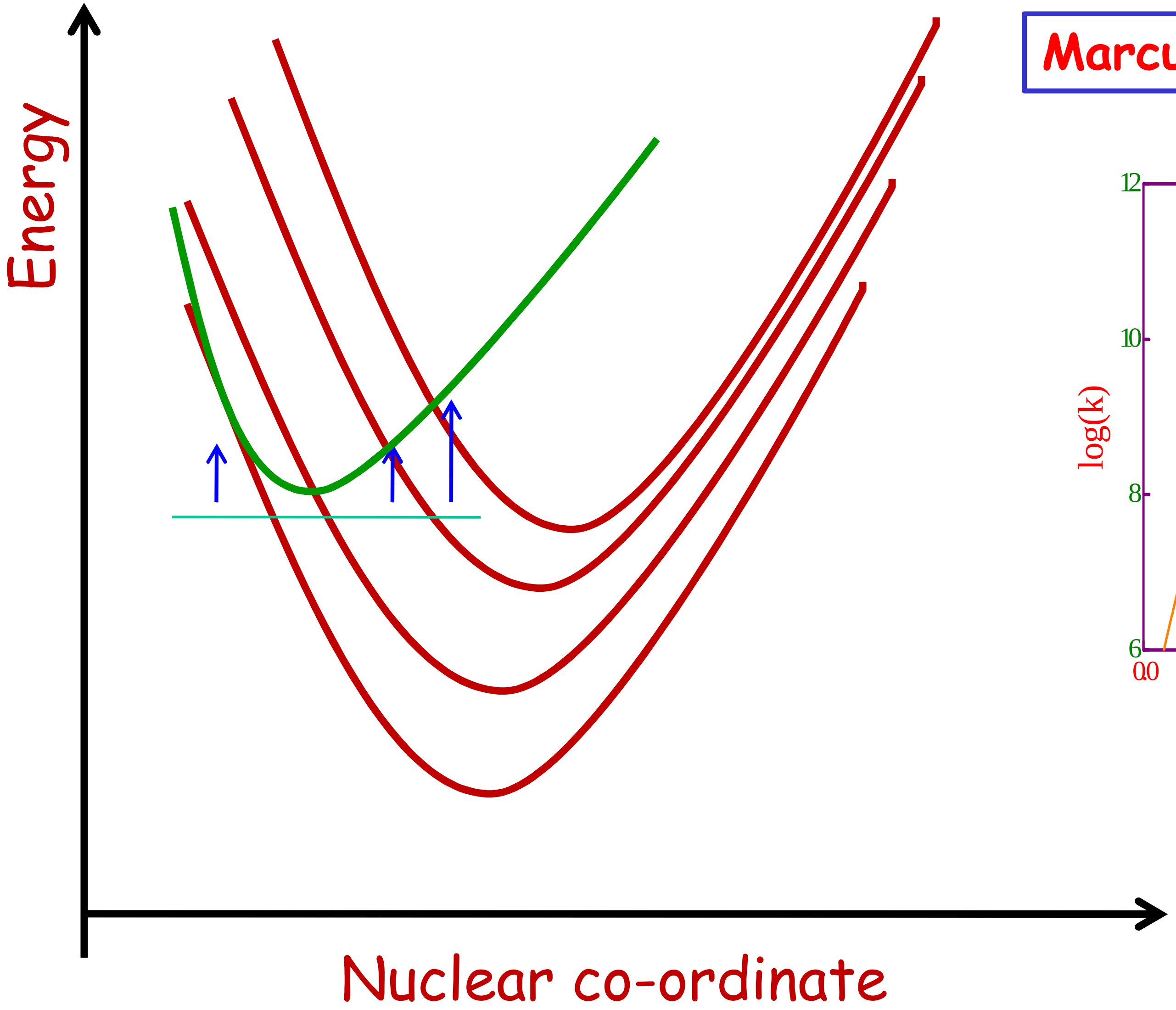


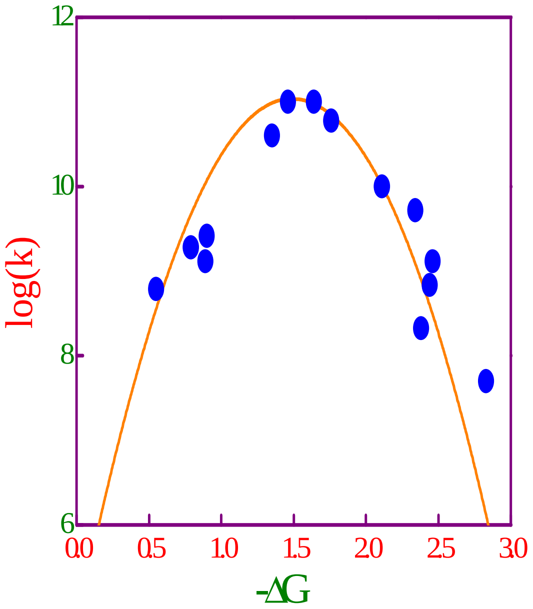
Marcus Inverted Region

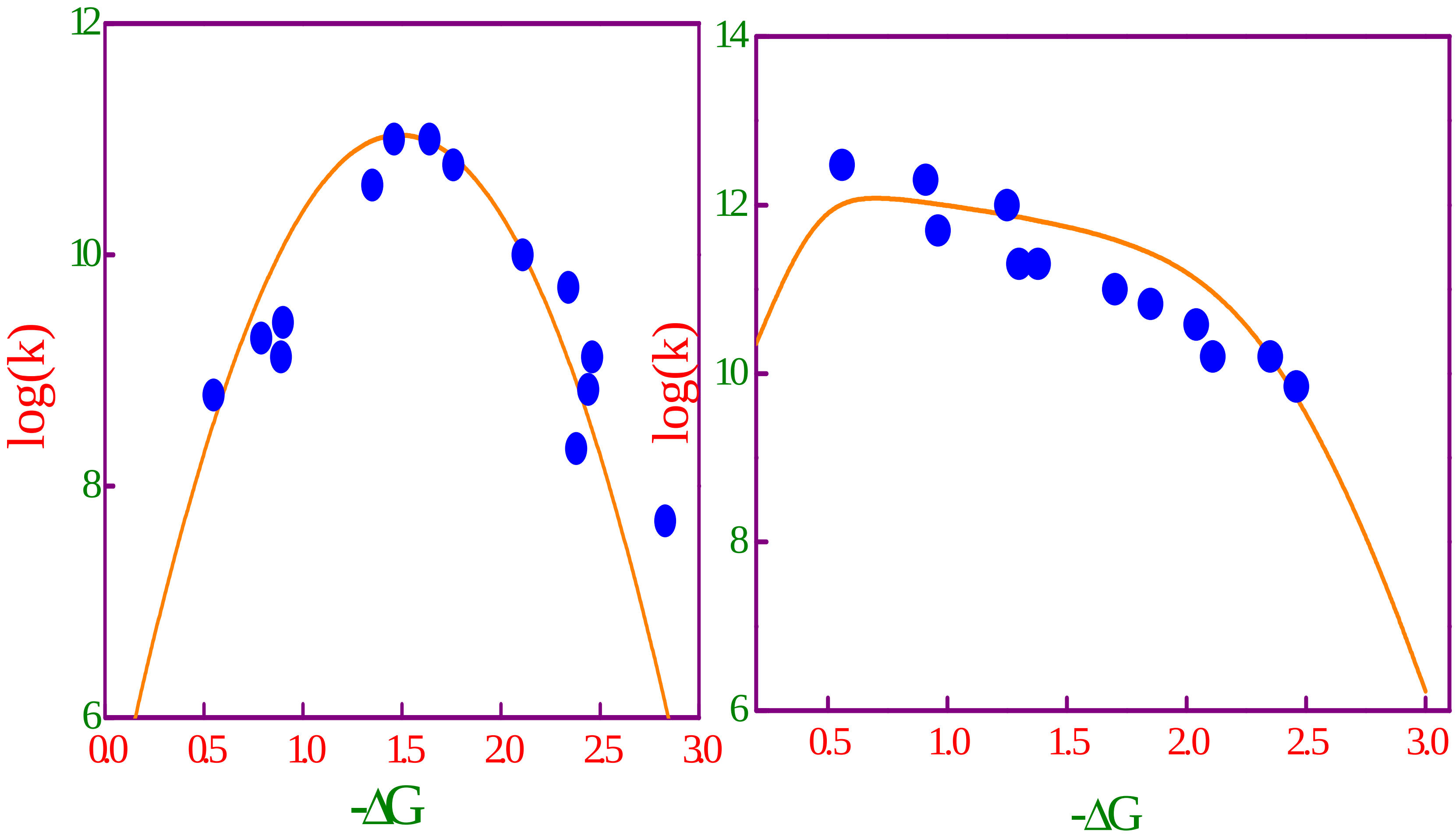


Free Energy Gap dependence of Activation energy & ET Rate



Marcus Inverted Region





Charge recombination reactions
in solvent separated ion pair

Charge recombination reaction
in contact ion pairs

One-dimensinal description of the Two-dimensional Electron Transfer Reactions (ET)

Shown are the potential energy of the surface of the reactants on one side of the transition state curve ABC, and those of the product on the other side.

ET takes place when $V^P(Q,X) = V^R(Q,X)$.

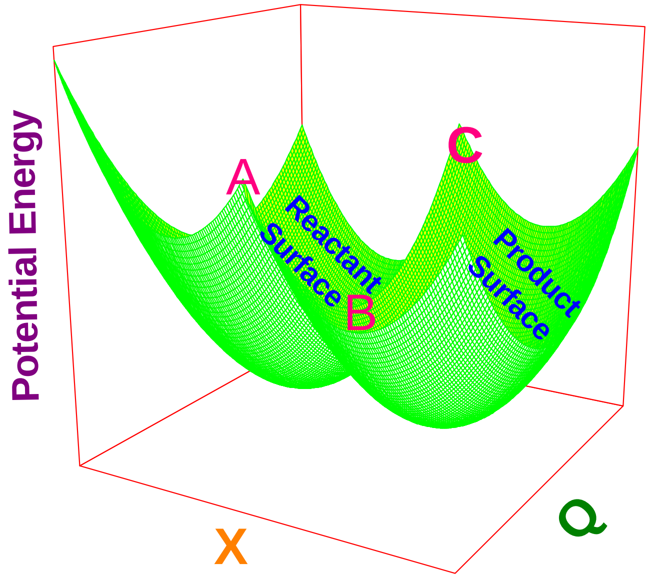
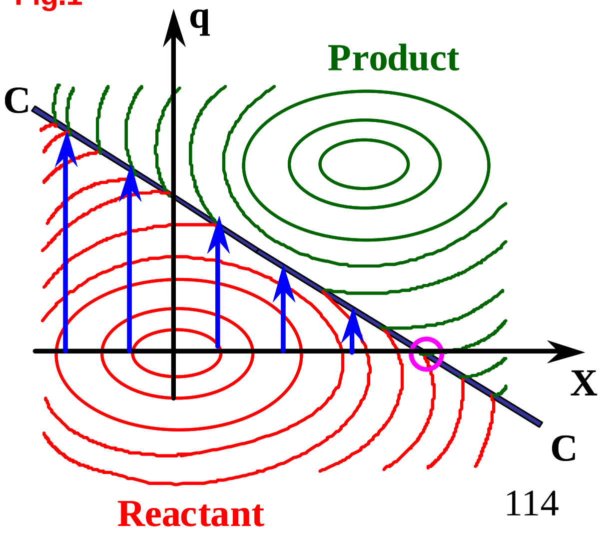


Fig.1



The relevant microscopic operator A for the ET reaction is taken as

$$A = V^P(Q,X) - V^R(Q,X) = \gamma$$

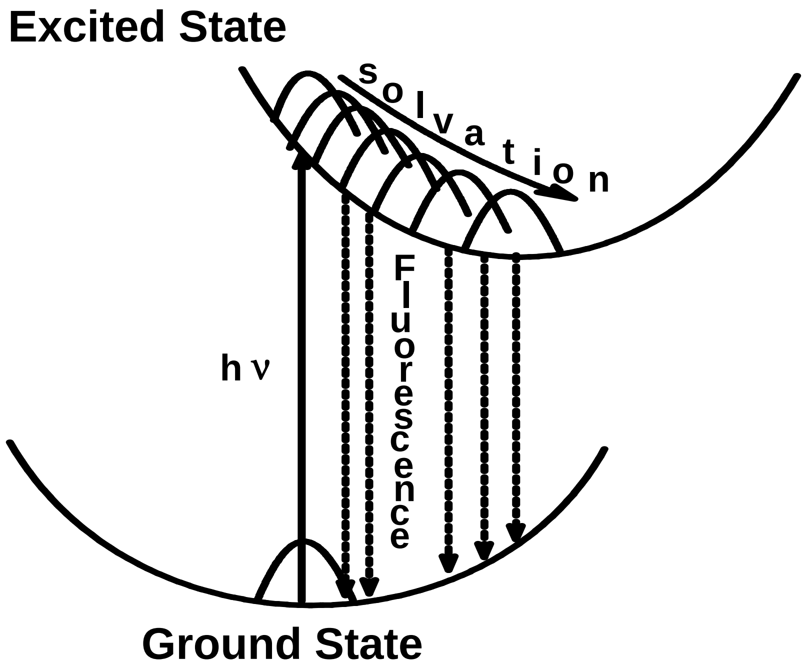
Potential energy

Reactant : $V^R(Q,X)=1/2\ aQ^2+ 1/2\ X$

Product: $V^P(Q,X)=1/2\ a(Q-Q_0)^2+ 1/2\ (X-X_0)^2 + \Delta G$

Nonequilibrium Solvation Dynamics

The most straightforward way to study the solvation dynamics is via time dependent fluorescence Stokes shift. In this experiment, a solute probe is optically excited, leading to a non-equilibrium state of the surrounding molecules which subsequently undergo rotational and translational relaxation to adjust to the new charge distribution, leading to energy lowering of the excited solute-solvent system and hence red shift in the fluorescence spectrum.



Stokes shift function

S(t) = [ΔE(t)- ΔE(∞)]/[ΔE(0)- ΔE(∞)]

ΔE(t) is the energy gap between the ground and excited state.

Summary of density variables

•The density has reference to electron density in microscopic length scale, particle number density in mesoscopic scale, & also probability density for the end to end distance of polymer etc.

•Also considered is the probability distribution $P(\gamma,t)$ denoting the probability of any microscopic phase-space variable A (in general multi-dimensional) constrained to have a value γ.

•Thus, one can have a probability $P(E,t)$ for a system to have energy E at time t and have an energy diffusion equation and consider the one-dimensional dynamics for an otherwise multi-dimensional dynamical process.

Summary & Conclusion

- ➢ The objective, role and methodology of theoretical and computational chemistry highlighted.
- ➢ Theory, modeling & simulation at different length and time scales discussed.
- ➢ Density Concept is shown to play an important role in providing a unified framework for Modelling at all length scales: *Electronic, Atomistic, Continuum Simulation*
- ➢ Versatility of DFT enhanced through Density quantities other than the electron density or number density
- ❑ Illustrative Applications:

Quantum:

- ▪ Coarse-grained density in modeling Molecules, Materials & Intermolecular Interaction
- ▪ Carbon nano Materials for H_2 adsorption
- ▪ Cluster-assembled materials

Classical:

- ▪ Structural and Dynamical Aspects of Soft Matter at interfaces

Summary & Conclusion

Density Concept plays an important role in providing a unified framework for Modelling at all length scales: *Electronic, Atomistic, Continuum Simulation*

Quantum DFT: Effective one-particle Schrodinger
equation: Modelling with electron density
Application: Coarse-grained density in modeling
Molecules, Materials & Intermolecular Interaction ,
Carbon nano Materials for H_2 adsorption,
Cluster-assembled materials

Classical DFT: Effective Boltzmann type distribution
with density-dependent effective potential:
Modelling with particle number density
Examples: Structural and Dynamical Aspects of Soft Matter at interfaces .

Dynamical Phenomena: Density based approach useful

Versatility of DFT enhanced through Density quantities other than the electron density or number density

Proposal of Charles Darwin

This proposal is for the P.I., a geologist by training, to solve the problem of speciation

Method: Collect every possible fact and formulate an all-inclusive theory.

Duration: 20 years

Proposal of Albert Einstein

This proposal is for the study of the nature of Space and time.

Method: Conduct thought experiments in armchair, supported by abstract mathematics.

Duration: 1 Lifetime

Figure 3. Charles Darwin engaged in the arcane and almost lost art that today we would label *thinking*. Illustration by Richard Loehle.

What would have happened if Darwin and Einstein as young Men had needed to apply for research grant ?

Theoretical Chemistry Research in BARC

- The primary goal of theoretical chemistry is to provide an understanding and rationalization of the observed chemical phenomena as well as to predict new phenomena by developing concepts or performing computations with the help of the available theoretical tools, modeling strategies or simulation techniques.
- Formulation of new and more powerful theoretical, modeling or simulation techniques thus forms an ongoing and integral part of research activities in theoretical chemistry.
- The main focus of the theoretical chemistry research in BARC can be broadly classified as follows.

A. Development of new formalisms / implementation of existing formalisms:
B. Fundamental & interpretive aspects of quantum & statistical mechanics:
C. Structure & properties of materials: From molecules to materials:
D. Dynamics of physicochemical phenomena:
E. Computer simulation (classical as well as quantum):

Theoretical Chemistry Research in BARC (contd)

A. Development of new formalisms and implementation of the existing formalisms:

- The theoretical tools of interest to us have been the (i) Density functional theory (ii) Hartree-Fock and post Hartree-Fock ab-initio electronic structure theory (iii) Integral equation theory for liquid structure (iv) Mode coupling theory of diffusivity in liquids (v) Time-dependent density functional theory, and (vi) Molecular hydrodynamics.

B. Fundamental and interpretive aspects of quantum and statistical mechanics:

- The central theme here has broadly been to describe many-particle systems (quantum or classical) within the framework of a single-particle picture, to provide important generalizations with regard to fundamental developments as well as applications of vital chemical significance, thus widening the scope of applicability immensely.

Theoretical Chemistry Research in BARC (contd)

C. Structure and properties of materials: From molecules to materials:

- One of the objectives here is materials modeling at different length scales, viz. micro-, meso- and macro-scopic length scales. The study covers both quantum and classical systems spanning over the entire range of electronic structure of quantum systems, including atoms, molecules, clusters, nanomaterials and solids on the one hand and the structure and properties of soft condensed matter including simple as well as complex fluids such as electrolytes, polymers, colloids, surfactants, micelles and other self-organized assemblies, on the other.

Theoretical Chemistry Research in BARC (contd)

D. Dynamics of physicochemical phenomena:

- The objective here is to understand the dynamics of processes covering different time scales, viz. slow, fast as well as ultrafast time scales. Besides the usual chemical reactions in gas phase as well as condensed phase, the study also covers electron and proton transfer processes, electron solvation, barrier crossing processes in general, polymer folding processes, transport phenomena such as diffusion in fluid mixtures etc.

E. Computer simulation (classical as well as quantum):

- One attempts here to predict the structure and dynamics of model as well as real systems using the classical simulation techniques such as Monte Carlo or Molecular Dynamics and also the ab-initio Car-Parrinello quantum simulation technique.

Concluding Remarks

- The research described here is driven by a desire to understand the equilibrium structure (“why are things the way they are”) as well as the dynamics (“from being to becoming”) of physico-chemical systems and phenomena respectively.
- The objective has been to develop new computationally economic and conceptually simple theoretical formalisms and also unify, interlink and strengthen the various diverse approaches in the theory of structure and dynamics of atoms, molecules, solids and liquids, aiming at a common unified view of the microscopic and macroscopic world.
- The field of theoretical chemistry is now fairly interdisciplinary having close interconnections with other areas such as theoretical and condensed matter physics, theoretical biology, computational materials science and chemical engineering.
- Work is in progress in many of the interdisciplinary areas including supramolecular chemistry, molecular electronics, quantum dot, nanomaterials, proten folding, single molecule spectroscopy etc.

- “Choice of right problems with right & meaningful questions to answer” makes the difference irrespective of whether the work involves experimental or theoretical investigations or both.

:Some Common Misconceptions:

- Studies based on experiments are automatically important and relevant, while the same based on theoretical or computational investigations are mostly irrelevant.
- Theoretical chemistry research is difficult. Too much mathematics.
- Theoretical chemistry research is very easy. Just run a software.

:Correct Perceptions:

- The importance, relevance or actual value of a research project depends solely on the actual nature of the problem and can be judged only by looking closely at its aims, objectives and outcome.
- The tag “Theoretical, computational or experimental” merely refers to the tool used in the study. An experimental investigation may also be of very routine and mundane type carrying no significance whatsoever, while a theoretical study may be of utmost importance *or vice versa.*
- Trivial studies may be easy in any field, but meaningful, nontrivial and significant research in any field is never easy.

:PROPOSAL:

- Have a synergy between theory, computation and experiment in all branches of chemical & allied sciences for best conceptualization and successful implementation of a research programme.
- A Seamless & interdisciplinary approach: Strength of each other is utilized to visualize significant research problems & their solution
- Interesting experimental results may be subjected to theoretical interpretation or computational support.
- Interesting theoretical predictions can also be utilized for planning new experiments to verify them.

- Two faces of the same coin and should be dealt with equal care, respect & consideration for support and distribution of resources
- Theoretical chemists are in no way less concerned with the need to contribute significantly to the growth & success of the objectives and programmes of the Department & Society at large.
- Success through mutual trust, help and collective planning is worth
- Live in harmony with dignity and independence (interdependence), building up an atmosphere conducive to creative research.

Theoretical Chemistry Research in TCS, BARC
Peer Recognition (National & International)

- Fellow, Indian Academy of Sciences, Bangalore: 1
- Fellow, Indian National Science Academy, New Delhi: 1
- Fellow, National Academy of Sciences, Allahabad: 2
- Fellow, The World Academy of Sciences (TWAS), Trieste, Italy: 1
- Fellow, Maharashtra Academy of Sciences, Pune: 2
- The World Academy of Sciences (TWAS) Prize in Chemistry: 1
- Indian National Science Academy Young Scientist Medal: 1
- Indian Science Congress Young Scientist Medal: 2
- Chemical Research Society of India Silver Medal: 1
- DAE Excellence Awards: 5
- Mentor, Indian Team for International Chemistry Olympiad for 2 consecutive years: 2