The world of nanocrystals: Theory of single and collective properties

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Why?

Storage devices (Murray, Sun and others)

Solar cells (Grätzel, Alivisatos, and others)

Molecular electronics (Alivisatos, McEuen, Park and others)

Lasers, LEDs (Banin, Bawendi, Alivisaots and others)

Structural design and bio-labeling (Mirkin, Alivisatos and others)
Part I

- What are nanocrystals?
  - Physical properties
  - Mechanical properties

- Electronic structure of nanocrystals
  - Bulk band structure
  - Kronig-Penny model
  - Effective mass approximation
  - K dot P method
  - Luttinger-Kohn and Kane models
  - Semiempirical pseudopotential method

- Results from the Rabani group

Part II

- Self Assembly - Experiments
  - Formation of disks and stripes
  - Formation of rings
  - Spinodal-like patterns

- Lattice gas approach
  - Model Hamiltonian
  - Dynamics
  - Length scales

- Results
  - Homogeneous evaporation
  - Inhomogeneous evaporation
  - Time scales and growth exponents
  - Self-similarity
Semiconductor nanocrystals, also known as “quantum dots,” maintain the crystalline structure of the bulk. However, due to the finite size of these quantum dots the physical properties of these materials may change significantly compared to the bulk.

- Band gap and optical properties
- Radiative lifetimes and blinking
- Charging energies
- Melting temperature
- Phase transitions
- High surface/volume ratio

Rabani group
Structural Phase Transitions

Multiple hysteresis cycles showing the unit cell volumes of the six-fold and four-fold phases vs. pressure (Alivisatos group).

Proposed mechanism of sliding planes for the pressure induced phase transition (Alivisatos group).

Wurtzite to rock salt transformation pressure vs. size of CdSe nanocrystals (Alivisatos group).
Optical Properties

InAs nanocrystals (Banin group)

CdSe nanocrystals (Bawendi group)
Electrons and Nanocrystals: Effective mass approximation to pseudopotential methods
Band Structure – Chemists View

\[ N = 2 \]

\[ N = 4 \]

\[ N = \infty \]
Kronig-Penney Model

The solution to the Schrödinger equation for a periodic potential must be of the form (Bloch):

\[ \psi_k(x) = u_k(x) \exp(ikx) \]

where \( u_k(x) = u_k(x + a) \) has the period of the crystal lattice.

The solution to the Kronig-Penny model is

\[ \psi_a(x) = Ae^{iKx} + Be^{-iKx} \quad E = \frac{\hbar^2 K^2}{2m} \]
\[ \psi_b(x) = Ce^{Qx} + De^{-Qx} \quad E = U_0 - \frac{\hbar^2 Q^2}{2m} \]

The constant A, B, C, D are chosen so that the wave function and its derivatives are continuous. Using Bloch’s theorem we find:

\[ \frac{P}{K_a} \sin(Ka) + \cos(Ka) = \cos(ka) \]

For simplicity we took the limit \( b = 0, U_0 = \infty \) such that \( P = Q^2ba / 2 \) is finite.
Bands, Energy and Free Electrons

Plot of the solution of the Kronig-Penny model. The allowed values of the energy are given by those ranges of $Ka$ which the function lies between $\pm 1$. Other ranges are forbidden gaps in the energy spectrum.

If we plot the energy as a function of the wave number we observe regions of allowed states and regions of gaps.

- Metals
- Semiconductors
- Insulators
The band structure of Silicon and CdSe (zinc-blende). Silicon is an indirect-gap semiconductor while CdSe is a direct-gap semiconductor.

Near the band gap one can make a parabolic approximation, known as the effective mass approximation. This approximation is the simplest one used to explain the quantum confinement effect in semiconductor nanocrystals.
Quantum Confinement

Effective Mass Approximation (in the context of nanocrystals this approximation was introduced by Efros and Efors (1982), and Brus (1983))

\[ H = -\frac{\hbar^2}{2m_e} \nabla_{r_e}^2 + V(r) \nabla_h^2 - \frac{\epsilon^2}{4 |r_e - r_h|} \]

Zero’s order solution

\[ \Psi(r_e, r_h) = \phi(r_e)\phi(r_h) \]

In polar coordinates

\[ \phi(r_{e,h}) = \sqrt{\frac{2}{a^3}} \frac{j_{\ell_{e,h}}(\kappa_{n_{e,h},\ell_{e,h}}r_{e,h}/R)}{j_{\ell_{e,h}+1}(\kappa_{n_{e,h},\ell_{e,h}})} Y_{\ell_{e,h}m_{e,h}}(\theta_{e,h}, \varphi_{e,h}) \]

where \( \kappa_{n,\ell} \) are the zeros of the spherical Bessel function.
Artificial Atoms

Atoms to bulk

Quantum dot

The nanocrystal states are labeled by the quantum number $n_e \ell_e n_h \ell_h$. For example, $1S_e 1S_h$ similar to the notation used for atoms.
The First Exciton Energy

The first exciton

\[ E_{1S_e 1S_h} = E_g + \frac{1}{2} \left( \frac{\hbar \pi}{R} \right)^2 \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\varepsilon R} \]

In reduced units

\[ \Delta E_{1S_e 1S_h} = E_R \left( \frac{\pi a_B}{R} \right)^2 - \frac{1.8e^2}{\varepsilon R} \]

where \( E_R = \frac{\hbar^2}{2m_{eh} a_B^2} \) and \( a_B = \frac{\varepsilon\hbar^2}{m_{eh} e^2} \)
Confinement Regimes

Strong confinement

Intermediate confinement

Weak confinement

\[ a < a_B^e, a_B^h \]

\[ a_B^h < a < a_B^e \]

\[ a > a_B^e, a_B^h \]

<table>
<thead>
<tr>
<th>Material</th>
<th>( m_e )</th>
<th>( m_h )</th>
<th>( E_g ) (eV)</th>
<th>( a_B ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>0.13</td>
<td>0.45</td>
<td>1.84</td>
<td>5.5</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.98</td>
<td>0.16</td>
<td>1.17</td>
<td>4.6</td>
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<tr>
<td>InAs</td>
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<td>0.4</td>
<td>0.41</td>
<td>34.0</td>
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<tr>
<td>InP</td>
<td>0.077</td>
<td>0.64</td>
<td>1.42</td>
<td>9.5</td>
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<tr>
<td>GaAs</td>
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<td>0.082</td>
<td>1.52</td>
<td>14.0</td>
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<tr>
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<td>0.8</td>
<td>2.6</td>
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<tr>
<td>PbSe</td>
<td>0.07</td>
<td>0.06</td>
<td>0.28</td>
<td>46.0</td>
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</table>
The band structure of semiconductors is often more complicated than the parabolic effective mass approximation. While in many cases the conduction band is well approximated by the effective mass model, the valence band is not. Spin-orbit coupling, crystal field splitting, and intra-band coupling give rise to a much more complicated band structure.

Due to spin-orbit coupling the valence band is split into two bands, split-off band ($J=1/2$) and light and heavy hole bands ($J=3/2 J_m=\pm 1/2$, $J=3/2 J_m=\pm 3/2$). $J$ is the sum of envelop and spin angular momentum.

In some cases due to crystal field the light hole and heavy hole are further split.
K dot P Method

Due to the complexity of the real band structure more accurate quantum dot calculations require one to go beyond the simple effective mass approximation. One such approximation is based on the k dot p method. In this approximation the solution is expanded exactly around a particular point in k space. The single particle Schrödinger equation reads

$$\left( \frac{p^2}{2m} + V(r) \right) \psi_k (r) = E_k \psi_k (r) \quad \Rightarrow \quad \left( \frac{(p+k)^2}{2m} + V(r) \right) u_k (r) = E_k u_k (r)$$

We can partition the Hamiltonian into a k-independent term and a correction

$$H_0 = \frac{p^2}{2m} + V(r) \quad H_1 = \frac{k \cdot p}{m}$$

Using second order perturbation theory we find

$$E_{nk} = E_{n0} + \frac{k^2}{2m} + \frac{1}{m^2} \sum_{m \neq n} \frac{|k \cdot p_{nm}|^2}{E_{n0} - E_{m0}} \quad u_{nk} (r) = u_{n0} (r) + \frac{1}{m} \sum_{m \neq n} \frac{k \cdot p_{nm}}{E_{n0} - E_{m0}} u_{m0} (r)$$
Luttinger and Kohn, and Kane introduced a method that better describes the nonparabolicities of the band structure and can also be used to treat the case of degeneracy of bands. Their approach is based on combining the k dot p method with direct diagonalization of the Hamiltonian. Specifically, a small subset of bands (valence and conduction) are treated exactly by direct diagonalization of the Hamiltonian, while other bands are treated with in the second order perturbation approximation.

In the Luttinger-Kohn model (4x4 and 6x6), only interactions within the valence band are treated exactly, while Kane (8x8) treats the k dot p interactions within the valence and conduction bands together.

The Luttinger-Kohn and Kane models require as input the effective masses of electrons and holes, dispersion parameters, momentum matrix elements, and spin orbit splitting. In some cases (like wurtzite structure) crystal-field splitting is also required.
Luttinger-Kohn and Kane Models

Since the Bloch functions at $k=0$ form a complete set, one can expand the wave function as

$$\psi_n(r) = \sum_{n=1}^{N} \left[ \sum_k b_n(k) e^{ik \cdot r} \right] u_{n0}(r) = \sum_{n=1}^{N} F_n(r) u_{n0}(r)$$

where $F_n(r)$ is the envelop function. Inserting this into the Schrödinger equation yields

$$\sum_{n=1}^{N} \left[ \left( \varepsilon_{n,0} + \frac{\hbar^2 k^2}{2m^2} - \varepsilon_{n,k} \right) \delta_{n,m} + \frac{\hbar}{m} k \cdot P_{m,n} \right] b_n(k) = 0$$

Using the standard basis set at $k=0$ combined with perturbation theory the $8 \times 8$ $k$ dot $p$ Hamiltonian matrix has the form

$$H(k) = \begin{pmatrix} H_d(k) & R \\ -R^* & H_d^*(k) \end{pmatrix}$$

where the four terms are $4 \times 4$ matrices with quadratic $k$ dependence. The direct diagonalization of this matrix results in bands that are not parabolic.
More Accurate Methods

In many electronic structure theories one can write an effective single electron Hamiltonian for the valence electrons. An example is the widely used density function theory in the Kohn-Sham formulation:

\[ \left( -\frac{1}{2} \nabla^2 + V_{KS}(r) \right) \psi_n(r) = \epsilon_n \psi_n(r) \]

where the Kohn-Sham potential is given by

\[ V_{KS}(r) = V_{ps}(r) + V_{xc}(r) \]

The first term on the rhs is the angular momentum dependent non-local pseudopotential, and the second term on the rhs is the screened potential made of interelectron Coulomb, exchange, and correlation parts. This potential depends on the charge density of the electrons.

Since nanocrystals involve thousands of electrons it is not really practical to solve the Kohn-Sham equations for a realistic system (see Toledo and Rabani). Instead we will introduce approximations, based on the well known empirical pseudopotential method. This method has been developed by Cohen and coworkers and later by Chelikowsky and coworkers for bulk and surface systems. Ramakrishna and Friesner extended this approach to nanocrystals. Based on the empirical pseudopotential method Zunger and coworkers have developed a semiempirical approach, which is the one I describe here.
The semiempirical pseudopotential method involves two approximations:

1) The screened potential is replaced with the potential calculated for the bulk. The physical motivation behind this approximation is that the screening is nearly size independent.

2) Since DFT is an electronic structure method for the ground state, adjustments to the local part of the non-local pseudopotential are made to fit bulk band structure.

For a nanocrystals the Kohn-Sham potential is approximated by a sum of screened non-local atomic potentials that are independent of electron density

\[ V_{KS}(r) = \sum_{\alpha} V_{ps}^{sc}(r - R_{\alpha}) \]

and the resulting single particle Schrödinger equation can be solved using a variety of techniques. We have developed an out-of-core filter-diagonalization approach to solve it for huge nanocrystals (Toledo and Rabani).

\[ \left( -\frac{1}{2} \nabla^2 + \sum_{\alpha} V_{ps}^{sc}(r) \right) \psi_n(r) = \varepsilon_n \psi_n(r) \]
Band Gap of CdSe

The semiempirical pseudopotential method has been used for a variety of nanocrystals, including CdSe, CdTe, CdS, Si, Ge, InP, InAs, GaAs, and GaP. The calculations for the band gap of CdSe are shown in the figure. The solid black line are the results of the effective mass approximation. The purple circles are non-local pseudopotential calculations of Wang and Zunger, and the orange circles are the results of Rabani et al. The results are compared with the experiments of Bawendi and coworkers (green circles).
Exciton Fine Structure - InAs

Williamson and Zunger

Calculated absorption spectra for single InAs quantum dots with diameters of 23.9, 30.3, 36.6, and 42.2 Å.

The assignment of the peaks with respect to the k dot p theory is:

(a) $S_{3/2} \rightarrow S_{1/2}$
(b) $P_{5/2} \rightarrow S_{1/2}$
(c) $P_{5/2} \rightarrow S_{1/2}$
(d) $S_{5/2} \rightarrow S_{1/2}$
(e) $S_{7/2} \rightarrow S_{1/2}$
(h) $P_{5/2} \rightarrow P_{3/2}$
(i) $S_{7/2} \rightarrow P_{3/2}$
(k) $P_{7/2} \rightarrow P_{3/2}$
Effects of the Environment

When the nanocrystal is deposited in a dielectric environment an interesting phenomena occurs. For example, the nanocrystal valence band states shift to the surface of the particle depending on its dipole moment.

The normalized integrated probability of the lowest valence state along the z axis is shown in the figure. The blue, red, and green lines are for $\varepsilon = 1$, $\varepsilon = 2$, and $\varepsilon = 8$, respectively.

The spectrum of the particles are also influenced by the environment. For strong dielectric media and strong coupling to the nanocrystal, absorption into states well inside the band-gap occurs.
Statistical mechanics and nanocrystals: Experiments and theory of Self-Assembly
TEM micrographs revealing the size-dependent phase separation and opal formation of attracting alkylthiol-functionalized Au nanocrystals.

TEM micrographs revealing the spontaneous formation of clusters and stripelike arrays of alkylthiol passivated Ag nanocrystals.

Wetting the Substrate

TEM images of 45 Å diameter dodecanethiol-capped gold nanocrystals condensed onto a carbon substrate by evaporating the solvent. Nanocrystals were dispersed in chloroform (left panel) and 90:10 chloroform:ethanol (right panel) at equal particle concentrations prior to solvent evaporation.

Nonequilibrium Structures - Rings

Scanning electron micrographs of annular \textit{rings} formed from the metal nanocrystal spheres.


Ferrite nanocrystals dispersed in hexane and deposited on a TEM grid, following under air.

Disks, Ribbons, and Cracks

Liquid tapping mode AFM height images of 4 nm CdSe nanocrystals at the HOPG - chloroform interface. A-C chloroform solutions: D, E hexane solutions. (F) 10% methanol 90% chloroform solution.

Spinodal Decomposition

\[ H = -\varepsilon_1 \sum_{\langle ij \rangle} l_i l_j - \mu \sum_i l_i \]
Phase separation dynamics from Monte Carlo simulations. The results are for conserved order parameter, with $R(t) \propto t^{1/3}$. For non-conserved dynamics the growth of domains scales as $R(t) \propto t^{1/2}$. 

Movie
Lattice Gas Model

Nano-nano scale with $d$.
Nano-liquid independent of $d$.

$$H = -\varepsilon_l \sum_{\langle ij \rangle} l_i l_j - \mu \sum_i l_i - \varepsilon_n \sum_{\langle ij \rangle} n_i n_j - \varepsilon_{nl} \sum_{\langle ij \rangle} n_i l_j$$
**Parameters**

Solvophilic case $\varepsilon_l < \varepsilon_{nl} < \varepsilon_n$

Favor evaporation $\mu < -2\varepsilon_l$

Wet or dry interface?

$\Delta E / L = \varepsilon_l + \varepsilon_{nl} + \mu$

$\Delta E = 5\varepsilon_{nl} - 3\varepsilon_n - 2\varepsilon_l$

$\exp(\Delta E / k_B T)$
Homogeneous Evaporation

Left panels show theoretical calculations of various morphologies of the self-assembly of nanocrystals in solution at 30%, 40% and 60% coverages for panels (a), (b), and (c), respectively. The fast evaporation in panel (a) leads to the formation of smaller domains, while slow evaporation in panels (b) and (c) lead to the formation of larger domains. All cases are for rapid nanoparticle mobility, the liquid completely wets the surface of the nanocrystal domains, and its evaporation is homogeneous.

Right panels show corresponding experimentally observed morphologies for CdSe nanocrystals for similar coverages.

Movie
Comparison between theory (panels a-c) and experiment (panels A-C) for the self-assembly of PbSe nanocrystals in octane solution at low coverage. The nanocrystal layer is in bright color. Theory is performed under conditions of slow evaporation and high nanoparticle mobility. The liquid wets completely the surface of nanocrystal domains and evaporates homogeneously.
Size Distribution

Size distribution of disks for slow evaporation and high mobility of nanocrystals at different times. The solid curve is the result of Cluster Diffusion model. The results obtained from simulations indicate that Cluster Diffusion is the preferred mechanism of domain growth under homogeneous slow evaporation and rapid nanocrystal mobility. The simulation data doesn’t fit predictions based on Ostwald ripening mechanism (not shown).
Inhomogeneous Evaporation

Theoretical prediction of the evolution of fractal-like, flower network under conditions of rapid evaporation, low nanocrystal mobility, and low temperature. Nanocrystal coverage is 30%. Here, unlike the other cases shown so far, the liquid doesn’t wet completely the surface of the nanocrystal domains at long times.
Formation of rod-like network of nanoparticles under conditions of rapid evaporation, rapid nanocrystal mobility, and low temperature. Coverage of nanoparticles is 10%. Note that the final two panels are nearly identical, demonstrating that the network formation occurs rapidly, while network evolution occurs slowly. Again, the liquid doesn’t wet completely the surface of the nanocrystal domains at long times.
Comparison of theory (left panel) under conditions of rapid evaporation, intermediate nanocrystal mobility, and low temperature and experiment (right panel) performed in hexane solution showing formation of network of CdSe nanocrystals. Coverage of nanoparticles is 20%.
In some cases we observe that the domain size growth scales as:

\[ R(t) \propto t^\alpha \]

Would other lengths scale with \( R(t) \)? For example, would the nonequilibrium structure factor scale with \( R(t) \) in the same way it scales in binary phase separation (here \( d \) is the dimensions and \( F \) is a function):

\[ S(q; t) = R(t)^d F(q R(t)) \]

Simple lattice-gas models, such as the Ising antiferromagnet \((H=-J \sum S_i S_j, \ J<0)\) with spin-exchange dynamics, or the Ising ferromagnet \((H=-J \sum S_i S_j, \ J>0)\) with spin-flip dynamics behave this way.
Example for Self-Similarity

$t = 256$

$t = 65536$
Not Self-Similar

$t=256$

$t=65536$
Jerusalem and Tel Aviv
North and South
Rabani Group
Me as a Graduate Student
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