Density of states in locally ordered amorphous organic semiconductors: emergence of the exponential tails

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Outline

- Density of states in amorphous organic semiconductors.
- Electrostatic disorder: dipoles and quadrupoles.
- Local order.
- Emergence of the exponential tails.

Sources of energetic disorder in amorphous organic materials

1. Electrostatic disorder: randomly located and oriented dipoles (polar molecules) and quadrupoles (majority of the nonpolar molecules).

2. Conformational disorder: fluctuation of the molecular angles and bond lengths.

3. Various defects: impurities, boundaries of crystallites, etc.

In this talk only the electrostatic disorder (mostly, quadrupolar disorder) will be discussed.

Density of states in amorphous organic semiconductors

1. Gaussian DOS

$$p(U) \propto \exp\left(-\frac{U^2}{2\sigma^2}\right), \quad \sigma \simeq 0.1\text{eV}$$

Typical for the electrostatic disorder.

1. Exponential DOS:

$$p(U) \propto \exp\left(\frac{U}{U_0}\right), \quad U < 0$$

Typically, the exponential tails in organic semiconducturs are related to the effect of charges.

Electrostatic disorder: simplest models

For the simplest models we assume:

- A spatial lattice with sites occupied by randomly oriented dipoles or quadrupoles and lattice scale a
- No correlation in the orientations of dipoles/quadrupoles
- For dipoles charge-dipole interaction energy and rms disorder σ are

$$U(\mathbf{r}) = \sum_n \frac{e\mathbf{p}_n \cdot (\mathbf{r} - \mathbf{r}_n)}{\varepsilon |\mathbf{r} - \mathbf{r}_n|^3}, \quad \sigma = A_d \frac{epc^{1/2}}{\varepsilon a^2}$$

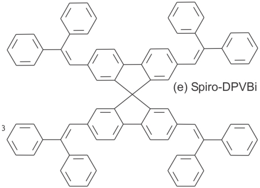
- For quadrupoles the corresponding energy and disorder are

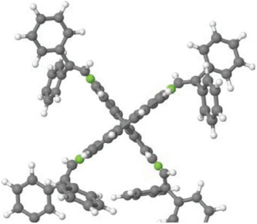
$$U(\mathbf{r}) = \sum_n \frac{eQ_n^{ij}(r - r_n)^i (r - r_n)^j}{\varepsilon |\mathbf{r} - \mathbf{r}_n|^5}, \quad \sigma = A_q U_0 c^{1/2}, \quad U_0 = \frac{eQ}{\varepsilon a^3}$$

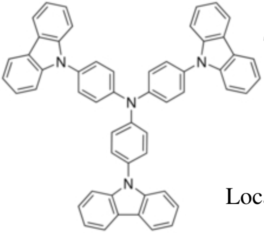
- Here c is a fracttion of sites occupied by dipoles/quadrupoles, and parameters $A_d \simeq 1$ and $A_q \simeq 1$ depend on the local arrangement of nearest neighbors.
- For both models $\sigma \simeq 0.1$ eV and the DOS has a Gaussian shape.

Why local order?

Spacious and asymmetric neighbor organic molecules cannot be arranged in the totally random independent way. Typical examples:

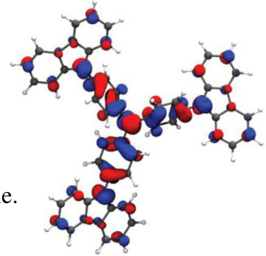






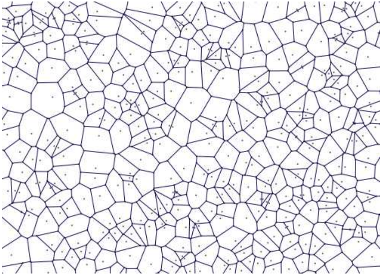
TCTA

Local order is inevitable.



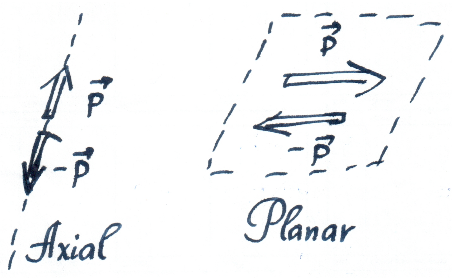
Local order: Voronoi model

We consider the simplest model of the local order in the quadrupole glass: the material is subdivided to domains and in each domain the quadrupoles are oriented in the same way, while the domain orientation is random. Domains are built as Voronoi cells:



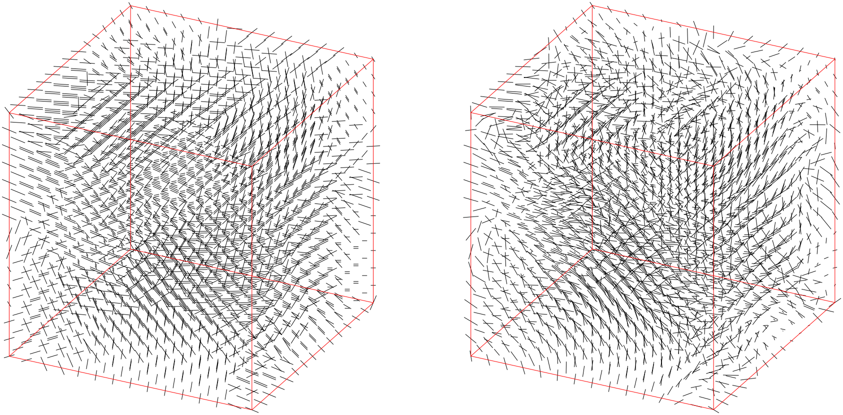
Seeding sites are selected at random, then Voronoi cells are drawn around each site. If L is the size of the basic cell (then applying the periodic boundary conditions), and N_s sites are chosen, then the average linear size of the cell is $l_a = L/N_s^{1/3}$.

Two basic types of quadrupoles



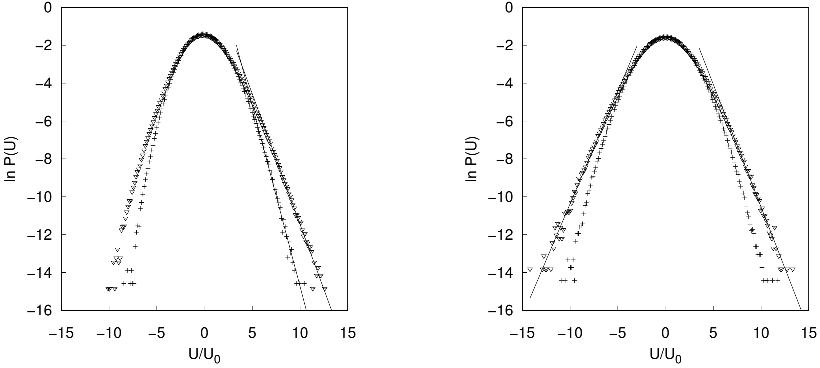
Each quadrupole may be arranged as a pair of antiparallel dipoles having equal dipole moments. For planar quadrupoles the DOS is typically symmetric around $U = 0$, while for the axial quadrupoles it is asymmetric.

Spatial distribution of quadrupoles



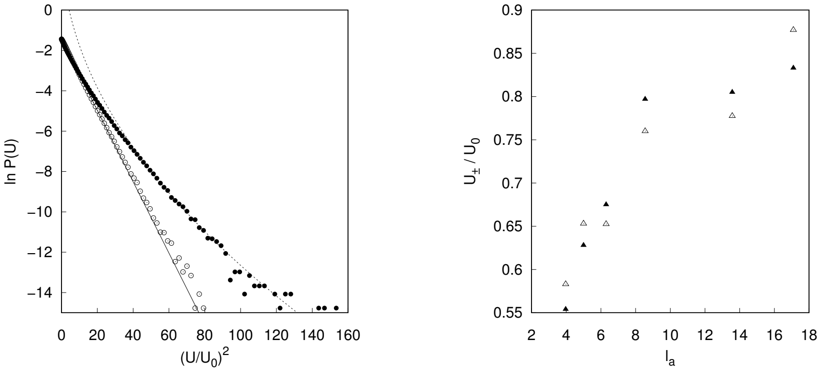
Distribution of the axes of quadrupoles for $15 \times 15 \times 15$ chunk of the axial Voronoi QG with $l_a = 5$ for sharp (left) and smoothed (right) boundaries between cells.

Resulting DOS



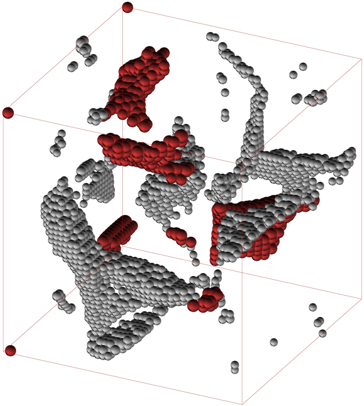
Emergence of the exponential tails of the DOS in the axial (left) and planar (right) quadrupole glass for $l_a = 2.9$ (+) and $l_a = 10$ (∇), $L = 50$. Central region of the DOS is approximately Gaussian with the same width irrespectively of l_a. Straight lines show the best exponential fits for the tails (plotted only for a well developed exponential asymptotics).

Resulting DOS - 2



(left) DOS for the axial QG with $l_a = 5$: low($\circ$) and high ($\bullet$) energy tails, correspondingly. Solid line shows the Gaussian fit for the central peak and the broken line shows the exponential fit; (right) Characteristic decay parameters of the exponential tails (for $U \to \pm\infty$) for planar ($\triangle$, here $U_+ \approx U_-$) and axial ($\blacktriangle$, only U_+ is shown) QG. Low energy tail for the axial glass is approximately Gaussian for rather high l_a.

Spatial distribution of the deepest/highest sites



(left) Distribution of the deepest (light grey) and highest (red) states ($|U| \geq 0.5U_{max}$, U_{max} is the maximal energy for this particular sample) in the $L = 50$ cubic sample of the axial Voronoi quadrupole glass for $l_a = 17$, high value of l_a was chosen for the better visibility of the structure. Radius of the ball is proportional to $|U|$. Concentration of the deepest/highest states at the interfaces (outer shells of the Voronoi polyhedra) is clearly visible.

Effect of the details of the ordering, dipolar semiconductors

- We may arrange the domains as an array of small cubes of equal size, the tails are practically the same (if the average sizes l_a are equal).
- Sharp boundaries between domains may be smoothed, the exponential tails becomes even more prominent.
- In the dipolar semiconductors the exponential tails develop if the nearest dipoles are oriented in the opposite directions (more restrictive condition).

Experimental evidence

Phys. Rev. Appl. **15**, 044050 (2021)
A. Stankevych et al., Density of States of OLED Host Materials from Thermally Stimulated Luminescence

For two amorphous materials having low dipole moment (i.e., this is probably the case of quadrupolar disorder) the formation of the exponential tails has been observed.

Conclusion

- Domains of the quadrupole molecules having approximately parallel orientations and linear size of $\simeq 5$ molecules produce the DOS having exponential tails.
- Details of the molecular arrangement are not important.
- Exponential tails develop for the dipolar materials if the nearby dipoles are oriented in the anti-ferroelectric manner.
- We may expect that this is quite common mechanism of the formation of the exponential tails in amorphous organic semiconductors.
- S.V. Novikov, *Density of states in locally ordered amorphous organic semiconductors: Emergence of the exponential tails*, J. Chem. Phys. 2021, 154(12), 124711.

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Thank you for your attention!