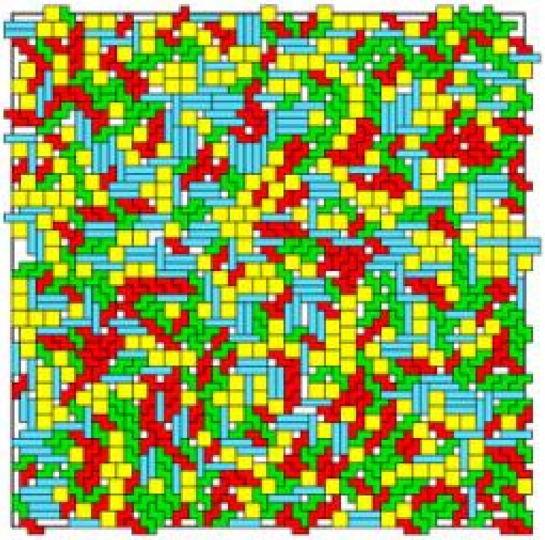
Birds of a feather: Study finds particles, molecules prefer not to mix

May 4 2009, By Tony Fitzpatrick



WUSTL chemists headed by Lev Gelb simulated the motions and behavior of particles on a lattice and found "birds of a feather stick together." It's plainly evident that, in this four-component mixture of squares, rods, S shapes and Z shapes, the shapes all make little clusters, rather than completely mixing together. Tetris, anyone?

(PhysOrg.com) -- In the world of small things, shape, order and orientation are surprisingly important, according to findings from a new study by chemists at Washington University in St. Louis.

Lev Gelb, WUSTL associate professor of chemistry, his graduate student Brian Barnes, and postdoctoral researcher Daniel Siderius, used computer simulations to study a very simple model of molecules on surfaces, which looks a lot like the computer game "Tetris." They have found that the shapes in this model (and in the game) do a number of surprising things.

"First, different shapes don't mix very well with each other; each shape prefers to associate with others of the same kind," Gelb says. "When you put a lot of different shapes together, they separate from each other on microscopic scales, forming little clusters of nearly pure fluids. This is true even for the mirror-image shapes.

"Second, the structures of the pure (single-shape) fluids are quite complex and not what we might have predicted. There is a very strong tendency for some of the shapes, like rods and S- and Z- shapes, to align in the same direction. Finally, how `different looking' the shapes are isn't a good predictor for how well they mix; it turns out that the hard-to-predict characteristic structures of the fluids are more important than the shapes themselves, in this regard."

The researchers used Monte Carlo computer simulations of a simple lattice model (think of the lattice as a checkerboard), on which are placed "tetrominoes," which are S-, Z-, L-, J-, T-, rod- and square-shaped pieces.

Gelb and his colleagues use simulations to develop an atomic-scale understanding of the behavior of complex systems. They want to understand how molecules and nanoparticles of different shapes interact with each other to gain a better understanding of self-assembly, which is important in the development of new, strong materials for one, and designed catalysts for another.

Lining up

Gelb says that there has long been interest in self-assembly and in designing things that will assemble into predictable structures. Most researchers try to hold simple shapes together energetically, using some sort of chemical lock and key, such as DNA or hydrogen bonds. But if the particles have more shape to them, surprising things can happen.

"People have known for a long time when you make round nanoparticles and deposit them on a surface and you do it well, they make a nice, crystalline lattice," Gelb says. "If you do mixtures of two sizes you can get a number of different patterns with them. But if the particles aren't round, if they are short rods or things with more structure, it gets much more complicated quickly, and there's much less known about that."

The results were published in the on-line edition of the journal *Langmuir* on April 27, 2009: pubs.acs.org/doi/abs/10.1021/la900196b .

The chemists also studied all 21 mixtures of two different shapes, as well as many combinations of three or more shapes.

"In all of the binary mixtures you get small-scale phase separation, which is counterintuitive," Gelb says. "It's not that the shapes repel each other. When there's no special repulsion between things or no stronger interaction between things of the same shape, you expect things to mix really well. In fact, that's not what happens."

Using ideas from classical thermodynamics and solution theory, the team was able to understand this separation using two different quantities. One is the virial coefficient, which measures the overlap between two shapes. They found that the shapes adopt alignments that minimize this overlap. Another is the volume of mixing. If you mix two liquids together, the volume of the mixture isn't necessarily the same as the volume of pure liquids you started with. In a mixture of water and ethanol, for instance, the volume of the mixture is smaller by about five percent than the sum of the original volumes. They found that in this model the volume always goes up when mixing different shapes.

Small world

"That's another indication that they don't mix well," Gelb says. "They take up more space when you mix them than when you allow them to be separate."

The model provides information on a very small world.

"If you think of the shapes as molecules sticking to a crystalline surface they would be a few Angstroms wide," says Barnes. "If you relate the model to nanoparticles, the shapes would be much larger, on the scale of tens of nanometers across."

In explaining the alignment phenomenon, Siderius offers the analogy of a roomful of people trying to circulate among each other.

"If they're all randomly placed, they'd bump shoulders frequently," he says. "But if they aligned a bit, everyone could move around more freely, which increases the entropy. In the past, we'd think of an ordered system as being low in entropy, but in this case the ordered state is high entropy."

Does it have anything to do with Tetris?

"Well, it suggests that one of the reasons the game is difficult is that the shapes don't fit together as well as we might think," says Gelb. "That, and they come down too fast."

Provided by Washington University in St. Louis (news : web)

Citation: Birds of a feather: Study finds particles, molecules prefer not to mix (2009, May 4) retrieved 24 April 2024 from
https://phys.org/news/2009-05-birds-feather-particles-molecules.html