

Two dimensional Gay-Berne molecules under the influence of an external field

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1 The Gay-Berne model

The molecules we model are organic molecules of ellipsoidal shapes, no free charges and interact via van der waals forces. The perfect model for that type of molecules is the Gay-Berne model. Nematogens are represented as ellipsoids that interact with a Lennard Jones type potential where the overlap strength and range parameters are functions of the orientations and the separation of the interacting molecules. The potential energy function reads,

$$u_{ij} = 4\epsilon_0\epsilon^\nu(\hat{q}_i, \hat{q}_j)\epsilon'^\mu(\vec{r}, \hat{q}_i, \hat{q}_j) \times \left[\left(\frac{\sigma_0}{r - \sigma(\vec{r}, \hat{q}_i, \hat{q}_j) + \sigma_0} \right)^{12} - \left(\frac{\sigma_0}{r - \sigma(\vec{r}, \hat{q}_i, \hat{q}_j) + \sigma_0} \right)^6 \right]$$

It is a more complicated Lennard Jones function because now, not just two points interact, but collections of points. Energy and distance now depend on the distance and the orientation of molecules. This equation refers to only two molecules but if we want to talk about a N collection of liquid crystals, the potential energy of the system is,

$$U = \sum_{i=1}^N \sum_{j>i}^N u_{ij} \quad (1)$$

What we want to do is to add an external field to that system. That field has a corresponding potential energy term that will be added to the Gay-Berne potential energy of equation 1.

2 Adding an external field

In the presence of an external field the modification in the total potential energy is simple,

$$U = \sum_{j>i}^N \sum_{i=1}^{N-1} u_{ij} - \sum_{j=1}^N V_j \quad (2)$$

The second term comes from the field and is given by,

$$\sum_{j=1}^N V_j = -V_0 \sum_{j=1}^N T_2(\hat{\Omega}_j \cdot \hat{x}) \quad (3)$$

Where the extra degree of freedom is $\phi_j = \arccos(\hat{\Omega}_j \cdot \hat{x})$, the angle that molecule j forms with the axis of the applied field, \hat{x} . The beautiful attribute (and computational convenience) of the new total potential energy is that it can be written as a function of the following scalars (and ONLY a function of those scalars),

$$U = \sum_{j>i}^N \sum_{i=1}^{N-1} u_{ij}(r, \hat{r} \cdot \hat{\Omega}_i, \hat{r} \cdot \hat{\Omega}_j, \hat{\Omega}_i \cdot \hat{\Omega}_j) + \sum_{j=1}^N V_j(\hat{\Omega}_j \cdot \hat{x}) \quad (4)$$

All of the corresponding forces and torques that act on every molecule can now be written as simple derivatives of equation 4 based on the well known chain rule. Given a function $h = h(x_1(t), \dots, x_n(t))$,

$$\frac{\partial h}{\partial t} = \sum_{i=1}^n \frac{\partial h}{\partial x_i} \frac{\partial x_i}{\partial t} \quad (5)$$

The force on the i -th molecule is given by,

$$\vec{f}_i = -\frac{\partial U}{\partial \vec{r}_i} = -\sum_{j \neq i} \frac{\partial u_{ij}}{\partial \vec{r}_i} \quad (6)$$

Notice how the field term is not important here since the potential energy coming from the field does not depend on any distance whatsoever. Previous group members (Layne and Yichen) have calculated the vector derivative in equation 6 and have implemented it in the code. Now we turn our attention to the torque that a Gay-Berne molecule experiences throughout the simulation. In order to calculate the torques we make use of the Allen-Germano strategy ([Allen and Germano \(2006\)](#)) where we evaluate the so-called auxiliary torque. The one coming from the field on molecule j will be written as,

$$\vec{g}_j = -\frac{\partial U}{\partial \hat{\Omega}_j} = -\frac{\partial U}{\partial \phi_j} \frac{\partial \phi_j}{\partial \hat{\Omega}_j} = -\frac{\partial U}{\partial \phi_j} \frac{\partial \phi_j}{\partial (\hat{\Omega}_j \cdot \hat{x})} \frac{\partial (\hat{\Omega}_j \cdot \hat{x})}{\partial \hat{\Omega}_j} \quad (7)$$

where we made use of the chain rule twice. Finally I figured out the direction of the auxiliary torque (the Achilles' heel of my last two reports) and it is given by the third term in the product,

$$\frac{\partial(\hat{\Omega}_j \cdot \hat{x})}{\partial(\hat{\Omega}_j)_\mu} = \frac{\partial}{\partial(\hat{\Omega}_j)_\mu} \sum_{\nu=\mu,k} x_\nu (\hat{\Omega}_j)_\nu = x_\mu \quad (8)$$

which means that,

$$\frac{\partial(\hat{\Omega}_j \cdot \hat{x})}{\partial \hat{\Omega}_j} = \hat{x} \quad (9)$$

The direction of the auxiliary torque is the same as the direction of the applied field. This derivation is the same with the calculation of the auxiliary torques coming from the inter molecular forces. When doing the actual calculation of the derivative it was assumed that the two components (ν and k) of the orientation are independent. We are allowed to do that since the length constraint $((\Omega_{j\mu})^2 + (\Omega_{jk})^2 = 1)$ has not been applied yet to that point. Similarly to solving equations of motion with a constraint (SHAKE algorithm), we treat the orientation vector as a free vector with independent components, then we calculate the auxiliary torque and finally impose the constraint. Going back to the derivation of the auxiliary torque we have,

$$\vec{g}_j = -\frac{\partial U}{\partial \phi_j} \frac{\partial \phi_j}{\partial(\hat{\Omega}_j \cdot \hat{x})} \hat{x} \quad (10)$$

The second term of the product,

$$\frac{\partial \phi_j}{\partial(\hat{\Omega}_j \cdot \hat{x})} = \frac{\partial \arccos(\hat{\Omega}_j \cdot \hat{x})}{\partial(\hat{\Omega}_j \cdot \hat{x})} = -\frac{1}{\sqrt{1 - (\hat{\Omega}_j \cdot \hat{x})^2}} \quad (11)$$

And the first term of the product is a derivative of the field part of the potential energy only,

$$\frac{\partial U}{\partial \phi_j} = \frac{\partial}{\partial \phi_j} \sum_{i=1}^N V_i = \partial \phi_j 2V_0 \sin 2\phi_j = 4V_0 \sin \phi_j \cos \phi_j \quad (12)$$

We need to express the above equation in terms of cosines. We can replace the sine function with either the negative or the positive square root,

$$\sin \phi_j = \pm \sqrt{1 - (\cos \phi_j)^2} \quad (13)$$

We will choose the negative expression so that the resulting force will drive molecules to orient parallel to the field's direction. In terms of the usual dot product,

$$\frac{\partial U}{\partial \phi_j} = -4V_0(\hat{\Omega}_j \cdot \hat{x}) \sqrt{1 - (\hat{\Omega}_j \cdot \hat{x})^2} \quad (14)$$

Thus,

$$\vec{g}_j = -4V_0(\hat{\Omega}_j \cdot \hat{x})\hat{x} \quad (15)$$

Finally, in the equations of motion we only use the perpendicular part of the auxiliary torque,

$$\vec{g}_j^P = \vec{g}_j - (\vec{g}_j \cdot \hat{\Omega}_j)\hat{\Omega}_j \quad (16)$$

That takes the simple form,

$$\vec{g}_j^P = -4V_0(\hat{x} \cdot \hat{\Omega}_j)(\hat{x} - (\hat{x} \cdot \hat{\Omega}_j)\hat{\Omega}_j) \quad (17)$$

and its modulus is,

$$|\vec{g}_j^P|^2 = |\vec{g}_j|^2 - (\vec{g}_j \cdot \hat{\Omega}_j)^2 = \left(\frac{\partial U}{\partial \phi_j}\right)^2 \quad (18)$$

The connection with what we said in our last discussion is now obvious: The "effective torque" you defined is the modulus of the perpendicular part of the auxiliary torque of Allen and Germano's strategy. Finally, a single liquid crystal molecule experiences torque coming from the other molecules and from the field. The intermolecular torque was not shown here in the report but can be found in [Allen and Germano \(2006\)](#). Overall the total molecular torque is,

$$\vec{g}_j = - \sum_{i \neq j} \left(\frac{\partial U}{\partial(\hat{r} \cdot \hat{\Omega}_j)} \vec{r}_{ij} + \frac{\partial U}{\partial(\hat{\Omega}_i \cdot \hat{\Omega}_j)} \hat{\Omega}_i \right) - 4V_0(\hat{\Omega}_j \cdot \hat{x})\hat{x} \quad (19)$$

We calculate the inter-molecular terms inside the sum based firstly on the distance between the tagged molecule j and the other molecules and secondly based on the other molecule's orientations with respect to the tagged molecule's orientation. After we are done with that part of the calculation with subtract the field term.

References

- M. P. Allen and G. Germano. Expressions for forces and torques in molecular simulations using rigid bodies. *Molecular Physics*, 104(20-21):3225–3235, 2006.