LJ-angle Virial Contribution
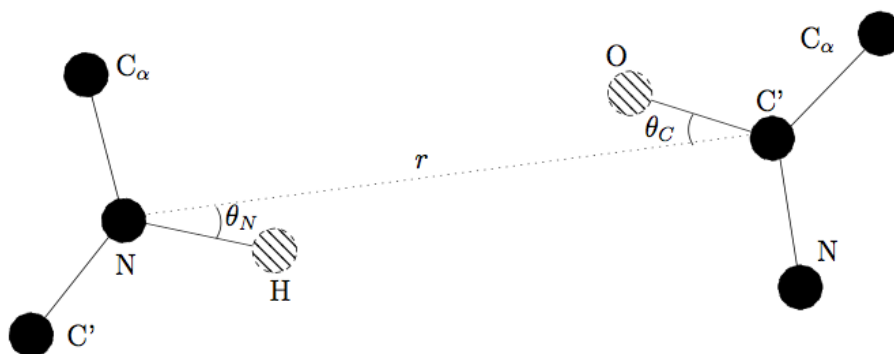
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Motivation

The ljangle potential is

$$V(r, \theta_N, \theta_C) = \epsilon \left[5 \left(\frac{\sigma}{r} \right)^{12} - 6 \left(\frac{\sigma}{r} \right)^{10} \right] \cos^2 \theta_N \cos^2 \theta_C \tag{1}$$

We will show here this potential's contribution to the scalar virial.

Figure 1: The hydrogen bond. Image taken from Bereau, T. and Deserno, M. *J. Chem. Phys.* **130** (2009), 235106 [BD09]. Copyright 2009, American Institute of Physics.

Introduction

We summarize here the method of Bekker, Berendsen, and van Gunsteren[1]. They show that a *strictly angle-dependent potential* does not contribute to the trace of the pressure tensor **W**. Their argument is as follows:

Three particles a, b, c define an angle ϕ between the vectors $\mathbf{r}_{ba}, \mathbf{r}_{bc}$. ϕ is invariant under translation of the system a, b, c, so

$$\boldsymbol{\nabla}_a \phi + \boldsymbol{\nabla}_b \phi + \boldsymbol{\nabla}_c \phi = 0 \tag{2}$$

Then they show that

$$\mathbf{r}_{ab} \cdot \boldsymbol{\nabla}_a \phi = 0 \tag{3}$$
$$\mathbf{r}_{cb} \cdot \boldsymbol{\nabla}_c \phi = 0 \tag{4}$$

$\boldsymbol{\nabla}_a \phi$ is the direction a must move to maximize the change in ϕ. This sits in the plane formed by a, b, c, and is perpendicular to $\mathbf{r}_{ab}$ because moving a in the direction along $\mathbf{r}_{ab}$ or normal to the plane a, b, c does not change ϕ. Therefore $\mathbf{r}_{ab} \cdot \boldsymbol{\nabla}_a \phi = 0$, and analogously $\mathbf{r}_{cb} \cdot \boldsymbol{\nabla}_c \phi = 0$.

Next, consider a system of N particles. We can define the shape of this system as the set of geometrical quantities that do not change under translation, rotation, or isotropic scaling of the system. Thus, the shape is given by the complete set of independent angles defined by particle triples. For a set of N particles, $2 + (N - 3) * 3 = M$ angles are required for a $N \geq 3$ particle system. Since every angle in our system can be computed from this complete

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[1] *Force and Virial of Torsional-Angle-Dependent Potentials*, Journal of Computational Chemistry, Vol. 16, No. 5, (1995)

set of independent angles, every angle-dependent potential V only depends on this set of independent angles, so $V = V(\phi_1, ..., \phi_M)$.

We compute

$$\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = \sum_{i=1}^{N} \mathbf{r}_i \cdot (-\boldsymbol{\nabla}_i V) \tag{5}$$

$$= \sum_{i=1}^{N} \mathbf{r}_i \cdot \left(-\sum_{\gamma=1}^{M} \frac{dV}{d\phi_\gamma} (\boldsymbol{\nabla}_i \phi_\gamma) \right)$$

$$= -\sum_{\gamma=1}^{M} \left(\frac{\partial V}{\partial \phi_\gamma} \sum_{i=1}^{N} (\mathbf{r}_i \cdot \boldsymbol{\nabla}_i \phi_\gamma) \right) \tag{6}$$

For specific γ, ϕ_γ in eq (6) is a specific angle from the complete set of independent angles we constructed above. Thus for any γ, only three $\boldsymbol{\nabla}_i \phi_\gamma$ terms in the sum running through N are nonzero, as ϕ_γ is defined by three particles (e.g. a, b, c).

Using equations (2), (3), (4), we can write

$$\sum_{i=1}^{N} (\mathbf{r}_i \cdot \boldsymbol{\nabla}_i \phi_\gamma) = \mathbf{r}_a \cdot \boldsymbol{\nabla}_a \phi_\gamma + \mathbf{r}_b \cdot -(\boldsymbol{\nabla}_a + \boldsymbol{\nabla}_c)\phi_\gamma + \mathbf{r}_c \cdot \boldsymbol{\nabla}_c \phi_\gamma \tag{7}$$

$$= \mathbf{r}_{ab} \cdot \boldsymbol{\nabla}_a \phi_\gamma + \mathbf{r}_{cb} \cdot \boldsymbol{\nabla}_c \phi = 0 \tag{8}$$

Thus a strictly angular potential contributes nothing to the scalar virial.

ljangle

Our potential is of the form

$$V = S(r)\Theta(\theta_1, \theta_2, ..., \theta_m) \tag{9}$$

(Technically the angular part is only dependent on two angles).

Following the previous approach,

$$\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = \sum_{i=1}^{N} \mathbf{r}_i \cdot (-\boldsymbol{\nabla}_i V) \tag{10}$$

$$= -\sum_{i=1}^{N} \mathbf{r}_i \cdot \left(\frac{\partial V}{\partial S} \boldsymbol{\nabla}_i S + \sum_{\gamma=1}^{M} \frac{\partial V}{\partial \Theta} \frac{\partial \Theta}{\partial \theta_\gamma} \boldsymbol{\nabla}_i \theta_\gamma \right) \tag{11}$$

$$= -\sum_{i=1}^{N} \mathbf{r}_i \cdot \frac{\partial V}{\partial S} \boldsymbol{\nabla}_i S - \sum_{i=1}^{N} \mathbf{r}_i \cdot \sum_{\gamma=1}^{M} \frac{\partial V}{\partial \Theta} \frac{\partial \Theta}{\partial \theta_\gamma} \boldsymbol{\nabla}_i \theta_\gamma \tag{12}$$

$$= \sum_{i=1}^{N} \mathbf{r}_i \cdot \tilde{\mathbf{F}}_i(r) - \sum_{\gamma=1}^{M} \frac{\partial V}{\partial \Theta} \frac{\partial \Theta}{\partial \theta_\gamma} \left(\sum_{i=1}^{N} \mathbf{r}_i \cdot \boldsymbol{\nabla}_i \theta_\gamma \right) \tag{13}$$

We have previously shown the parenthetical term to go to zero. Therefore, we have

$$\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = \sum_{i=1}^{N} \mathbf{r}_i \cdot \tilde{\mathbf{F}}_i(r) \tag{14}$$

$$\tilde{\mathbf{F}}_i(r) = -\frac{\partial V}{\partial S} \frac{\partial S}{\partial \mathbf{r}_i} = \Theta(\theta_1, \theta_2) \boldsymbol{\nabla}_i S(r) \tag{15}$$

In particular, since the radial part of this potential is only dependent of $\mathbf{r}_N, \mathbf{r}_{C'}$, for any given hydrogen bond,

$$\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = \mathbf{r}_N \cdot \tilde{\mathbf{F}}_N(r) + \mathbf{r}_{C'} \cdot \tilde{\mathbf{F}}(r) \tag{16}$$

$$= \Theta(\theta_1, \theta_2) \left[\mathbf{r}_N \cdot \boldsymbol{\nabla}_N S(r) + \mathbf{r}_{C'} \cdot \boldsymbol{\nabla}_{C'} S(r) \right] \tag{17}$$

$$= \Theta(\theta_1, \theta_2) S'(r) \left[\mathbf{r}_N \cdot \boldsymbol{\nabla}_N r + \mathbf{r}_{C'} \cdot \boldsymbol{\nabla}_{C'} r \right] \tag{18}$$

where $S' = \frac{\partial S}{\partial r}$.

It is useful to know that

$$\boldsymbol{\nabla}_i r_{ij} = \frac{\mathbf{r}_{ji}}{r_{ij}} \tag{19}$$

Therefore

$$\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i = \Theta(\theta_1, \theta_2) \frac{S'(r)}{r} \left[\mathbf{r}_N \cdot \mathbf{r}_{C'N} + \mathbf{r}_{C'} \cdot \mathbf{r}_{NC'} \right] \tag{20}$$

$$= \Theta(\theta_1, \theta_2) \frac{S'(r)}{r} \left[\mathbf{r}_N \cdot \mathbf{r}_{C'N} - \mathbf{r}_{C'} \cdot \mathbf{r}_{C'N} \right] \tag{21}$$

$$= \Theta(\theta_1, \theta_2) \frac{S'(r)}{r} \left[\mathbf{r}_{C'N} \cdot \mathbf{r}_{C'N} \right] \tag{22}$$

$$= \Theta(\theta_1, \theta_2) S'(r) r \tag{23}$$