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The case for keeping simulated clusters spherical.

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Several molecular modeling packages offer the option to solvate a molecule with a layer of solvent (usually water) of a certain thickness. The user then can run molecular dynamics on this cluster with the expectation that the a large portion of the solvent effect has been included into the system relatively economically. What has been left apparently unnoticed (with apologies to those by whom it has not) was that the surface tension of the cluster would introduce a bias toward more spherical shapes, therby introducing variations into the water layer thickness and possibly distorting the conformation of the solute. Clearly, neither of these effects are desirable.

To get an idea of the significance of this effect, I set up a simple model examining the deformation of a spherical droplet into an ellipsoidal one. The input of the model is

1. $V_{\rm o}$, the volume of a solvent molecule in the bulk (30 Å^3 for water);

2. α, a contraction factor ($\alpha \leq 1$) so that the volume of a molecule on the surface is $\alpha V_{\rm o}$;

3. N, the number of molecules in the droplet;

4. σ, the surface tension of the solvent (72 dyne/cm = 0.104 kcal/mol Å^2 at room temperature for water).

The work of deforming a sphere into an ellipsoid will be obtained from the change in the surface area.

The number of solvent molecules on the surface, $N_{\rm s}$, is estimated as

$$N_{\rm s} = S/[r_{\rm s}^2 1.5^{1.5}] \tag{1}$$

where $r_{\rm s}$ is the radius of the solvent molecule on the surface, by assuming that the surface S is covered with close-packed hexagons with inscribed sphere radius $r_{\rm s}$. For waters in the bulk, $r_{\rm s}$ is estimated (assuming FCC close packing) as

$$r_{\rm s} = (V_{\rm o}/2)^{1/3}/2^{1/2}. \tag{2}$$

Extending this estimate for solvents on the surface,

$$r_{\mathrm{s}} = (\alpha V_{\mathrm{o}}/2)^{1/3}/2^{1/2}. \tag{3}$$

The total volume to the droplet is

$$V = N_{\mathrm{s}}\alpha V_{\mathrm{o}} + (N - N_{\mathrm{s}}) * V_{\mathrm{o}} = [N + N_{\mathrm{s}} * (\alpha - 1)]V_{\mathrm{o}} \tag{4}$$

The volume of an ellipsoid of revolution is given as

$$V = 4\pi a^2 b/3 \tag{5}$$

where a, b are the lengths of the axes and its surface is

$$S = 2\pi ab[b/a + (a/c)\ln((b + c)/a)], \tag{6}$$

with

$$c = (b^2 - a^2)^{1/2}. \tag{7}$$

Defining $r = b/a$, this can be rewritten as

$$V = 4\pi a^3 r/3 \tag{8}$$

$$S = 2\pi a^2 r[r + \ln(r + (r^2 - 1)^{1/2})/(r^2 - 1)^{1/2}) \tag{9}$$

Substituting (1) and (3) into (4) eliminates N_{s} and r_{s}; substituting (8) into (9) eliminates a, leaving us with a system of two equations involving S and V:

$$V = \{N + (\alpha - 1) * S/[(\alpha V_{\mathrm{o}}/2)^{2/3}/2 \times 1.5^{1.5}]\}V_{\mathrm{o}} \tag{10}$$

$$S = 2\pi(4\pi/3)^{-2/3}V^{2/3}r^{1/3}[r + \ln(r + (r^2 - 1)^{1/2})/(r^2 - 1)^{1/2}) \tag{11}$$

For α=1, V becomes independent of S and thus the system is easily solvable analytically, and for $\alpha < 1$ the α=1 solution serves as the starting point of an iteration.

Tables 1 and 2 give the calculated surface free energies in kcal/mol using various α and r values for two droplets containing 1000 and 5000 waters, respectively, resulting in droplets

of radius 19 Åand 33 Å, respectively. The surface free energies were obtained by multiplying the surface value (in $Å^2$) by the surface tension, σ. Clearly, the effect is significant.

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Table 1: Estimated surface free energies of an ellipsoidal droplet of 1000 waters.

Axis ratio	Contraction factor	Surface free energy	Excess over spherical
1	1	485.0	0.0
1.05	1	501.2	16.2
1.1	1	517.6	32.7
1	.95	471.3	0.0
1.05	.95	486.6	15.3
1.1	.95	502.0	30.8
1	.9	457.2	0.0
1.05	.9	471.6	14.4
1.1	.9	486.1	28.9
1	.85	442.8	0.0
1.05	.85	456.3	13.5
1.1	.85	469.8	27.0

Table 2: Estimated surface free energies of an ellipsoidal droplet of 5000 waters.

Axis ratio	Contraction factor	Surface free energy	Excess over spherical
1	1	1418.0	0.0
1.05	1	1465.5	47.5
1.1	1	1513.5	95.5
1	.95	1394.4	0.0
1.05	.95	1440.3	45.9
1.1	.95	1486.7	92.2
1	.9	1369.8	0.0
1.05	.9	1414.0	44.2
1.1	.9	1458.6	88.8
1	.85	1343.9	0.0
1.05	.85	1386.3	42.4
1.1	.85	1429.2	85.3