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Application of Ewald summation to long-range dispersion forces

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Motivation

- Bulk simulations usually yield good results when cutoffs are large enough

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Motivation

- Bulk simulations generally yield adequate results when sufficiently large cutoffs are used
  - Tail corrections sufficient when cutoff r_c is large enough that $g(r) \sim 1$ for $r > r_c$
- Interfacial systems don't behave the same way
  - Density cannot be corrected
  - Surface tensions can be corrected, but accurate only if density is correct

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Methodology

- Ewald summation methods divide space into two regions:
  - A local neighborhood around a charge summed in real space
  - Remaining charges summed in reciprocal space
- Traditionally applied to $1/r$ potentials
  - Can be extended to other long-range potentials
    - $1/r^3$ (dipole)
    - $1/r^6$ (dispersion)

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Ewald sums

- Mathematically, Ewald sums are broken up using a switching function ϕ_m:

$$S_m = \sum_{i,j,L} \frac{A_{ij}\phi_m\left(\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L\right)}{\left|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L\right|^m} + \sum_{i,j,L} \frac{A_{ij}\left[1 - \phi_m\left(\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L\right)\right]}{\left|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L\right|^m}$$

- For $m = 1$: $\phi_1 = \mathrm{erfc}(r/\eta)$
- For $m = 6$:

$$\phi_6(r) = \left(1 + \left(\frac{r}{\eta}\right)^2 + \frac{1}{2}\left(\frac{r}{\eta}\right)^4\right)\exp\left(-\left(\frac{r}{\eta}\right)^2\right)$$

- η defines the cutoff between real and reciprocal spaces (mainly affects performance, not accuracy)

Formulae for r^{-6} energy and forces

$$
\begin{aligned}
E_6 &= \frac{1}{2\eta^6}\sum_{L,i,j} B_{ij}\left(1+a^2+\frac{a^4}{2}\right)\frac{e^{-a^2}}{a^6} \\
&+ \frac{\pi^{2/3}}{24V}\sum_{\mathbf{h}\neq\mathbf{0}} h^3\left(\pi^{1/2}\mathrm{erfc}(b)+\left(\frac{1}{2b^3}-\frac{1}{b}\right)e^{-b^2}\right) \\
&\times S_6(\mathbf{h})\,S_6(-\mathbf{h}) \\
&+ \frac{\pi^{2/3}}{6V\eta^3}\sum_{i,j} B_{ij} - \frac{1}{12\eta^6}\sum_i B_{ii},
\end{aligned}
$$

$$
\begin{aligned}
\mathbf{f}_{6,k} &= \frac{1}{\eta^{-8}}\sum_{L,j} B_{kj}(\mathbf{r}_k-\mathbf{r}_j-\mathbf{R}_L)(6a^{-8}+6a^{-6}+3a^{-4}+a^{-2}) \\
&+ \frac{\pi^{2/3}}{12V}\mathrm{Im}\left(\sum_{\mathbf{h}\neq\mathbf{0}} ib_k\exp(-i\mathbf{h}\cdot\mathbf{r}_k)h^3\left[\pi^{1/2}\mathrm{erfc}(b)+\left(\frac{1}{2b^3}-\frac{1}{b}\right)e^{-b^2}\right]S_6(\mathbf{h})\mathbf{h}\right)
\end{aligned}
$$

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Surface tension

For systems with slab geometry:

$$\gamma = \gamma_{sim} + \gamma_{tail}$$

$$\gamma_{sim} = \frac{L_z}{2}\left\langle p_\perp - p_\parallel \right\rangle = \frac{L_z}{2}\left\langle p_z - \left(\frac{p_x + p_y}{2}\right)\right\rangle$$

Tail correction for long-range dispersion forces:

$$\gamma_{tail} = \frac{\pi}{2}\int_{-\infty}^{\infty}\int_{-1}^{1}\int_{r_c}^{\infty} r^3\left(1-3s^2\right)\frac{\mathrm{d}U(r)}{\mathrm{d}r}g(r)\times \left(\rho(z)\rho(z-sr) - \left(\rho_G(z)\right)^2\right)\,\mathrm{d}r\,\mathrm{d}s\,\mathrm{d}z.$$

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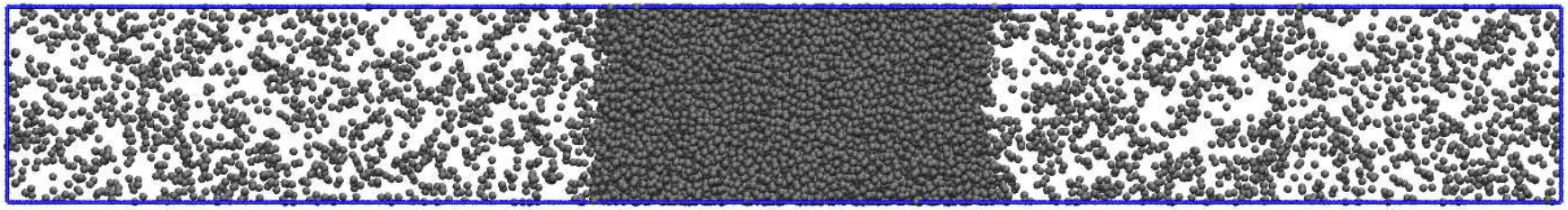
Lennard-Jones simulations



- *NVT* simulations of 16,000 LJ atoms
- T^* = 0.70, 0.85, 1.10
- Timestep $\Delta t = 0.005\tau$
- Equilibration for 1250τ, sampling for 3750τ
- Long-range forces treated with 2.5σ, 5σ, or 7.5σ cutoffs, or Ewald summation

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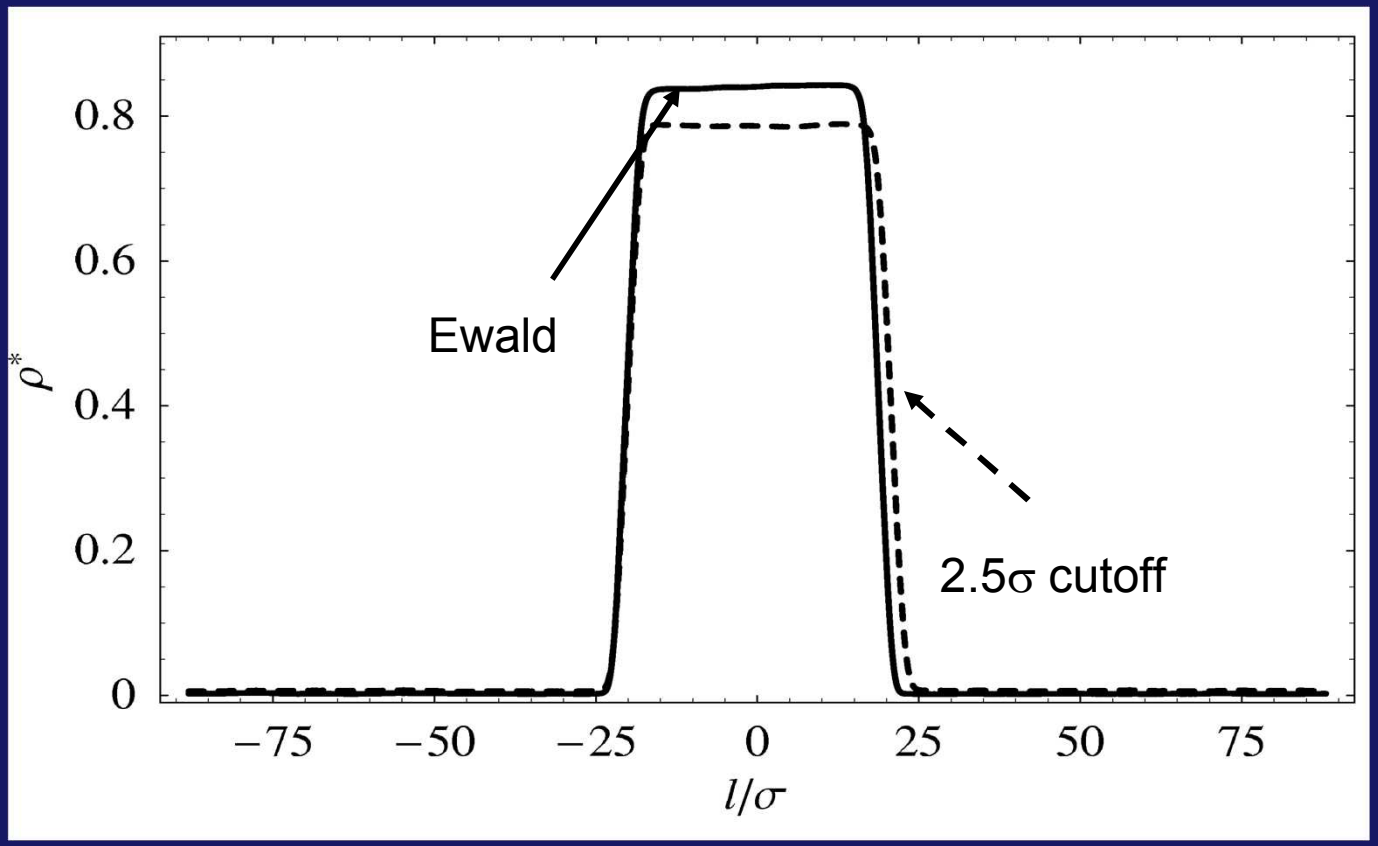
Lennard-Jones fluid: $T^* = 0.70$



Far from critical point, Ewald and cutoff yield similar density profiles

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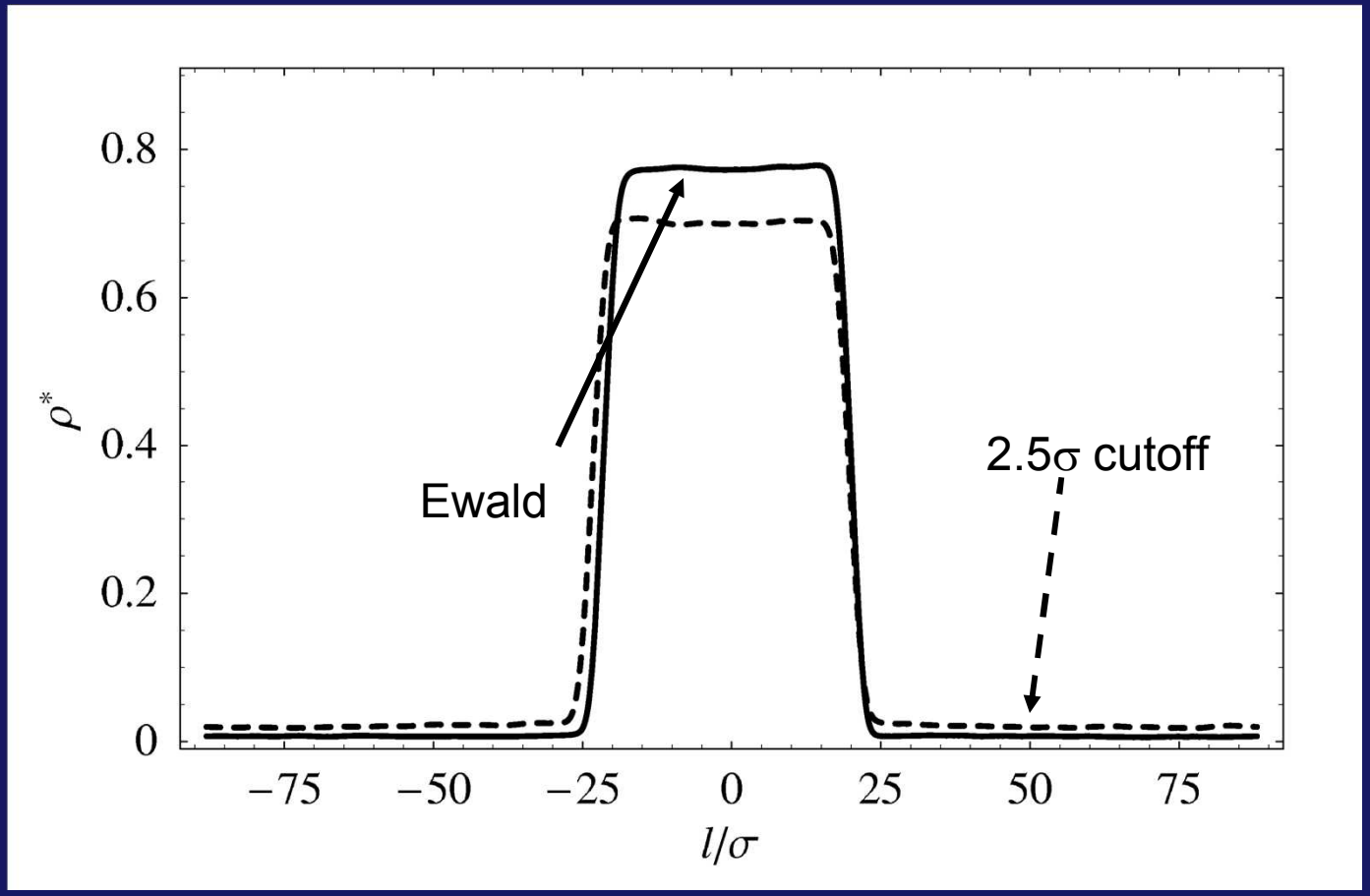
Lennard-Jones fluid: $T^* = 0.85$



Closer to critical point, Ewald and cutoff results start to diverge

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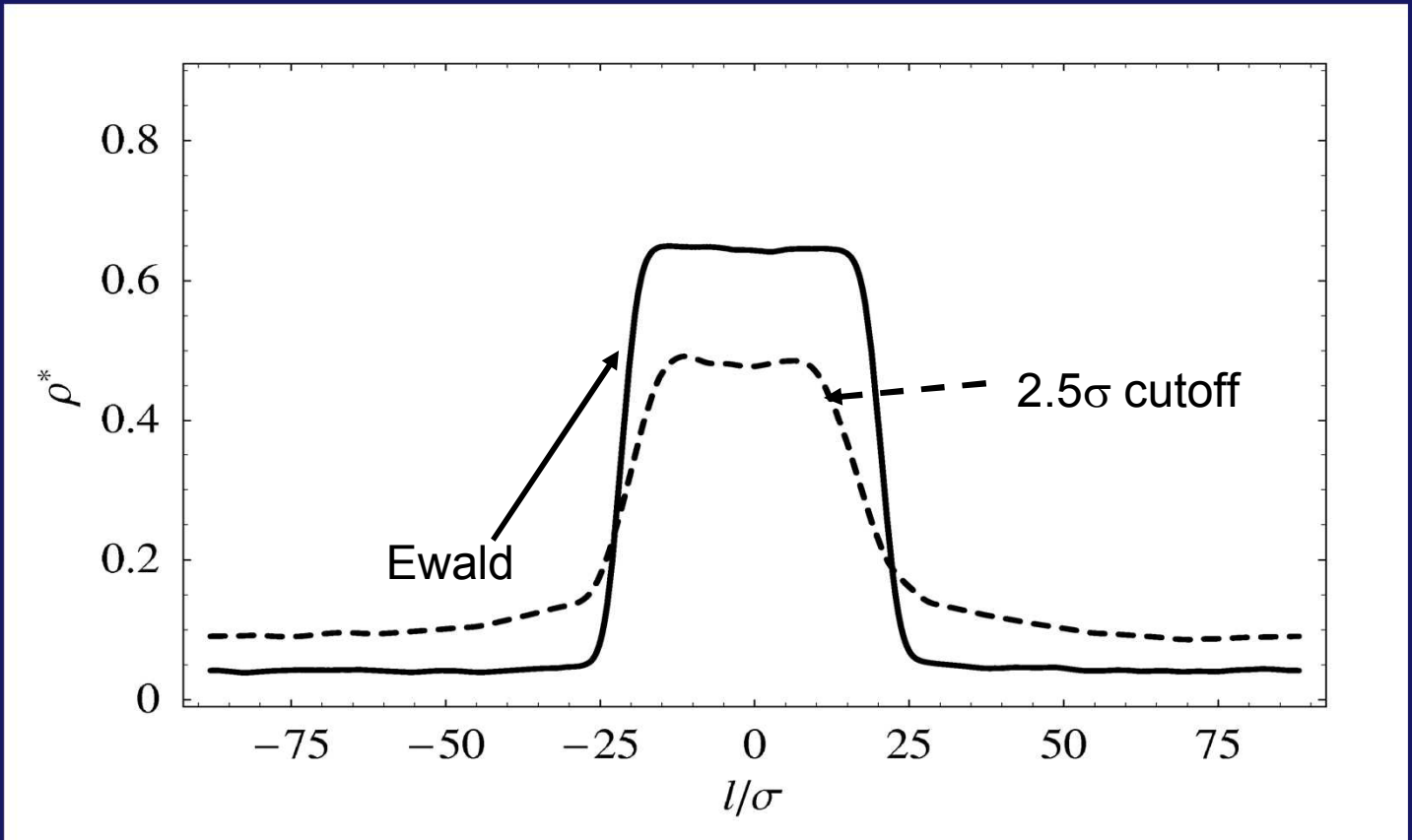
Lennard-Jones fluid: $T^* = 1.10$



Near critical point, Ewald summation needed for correct behavior

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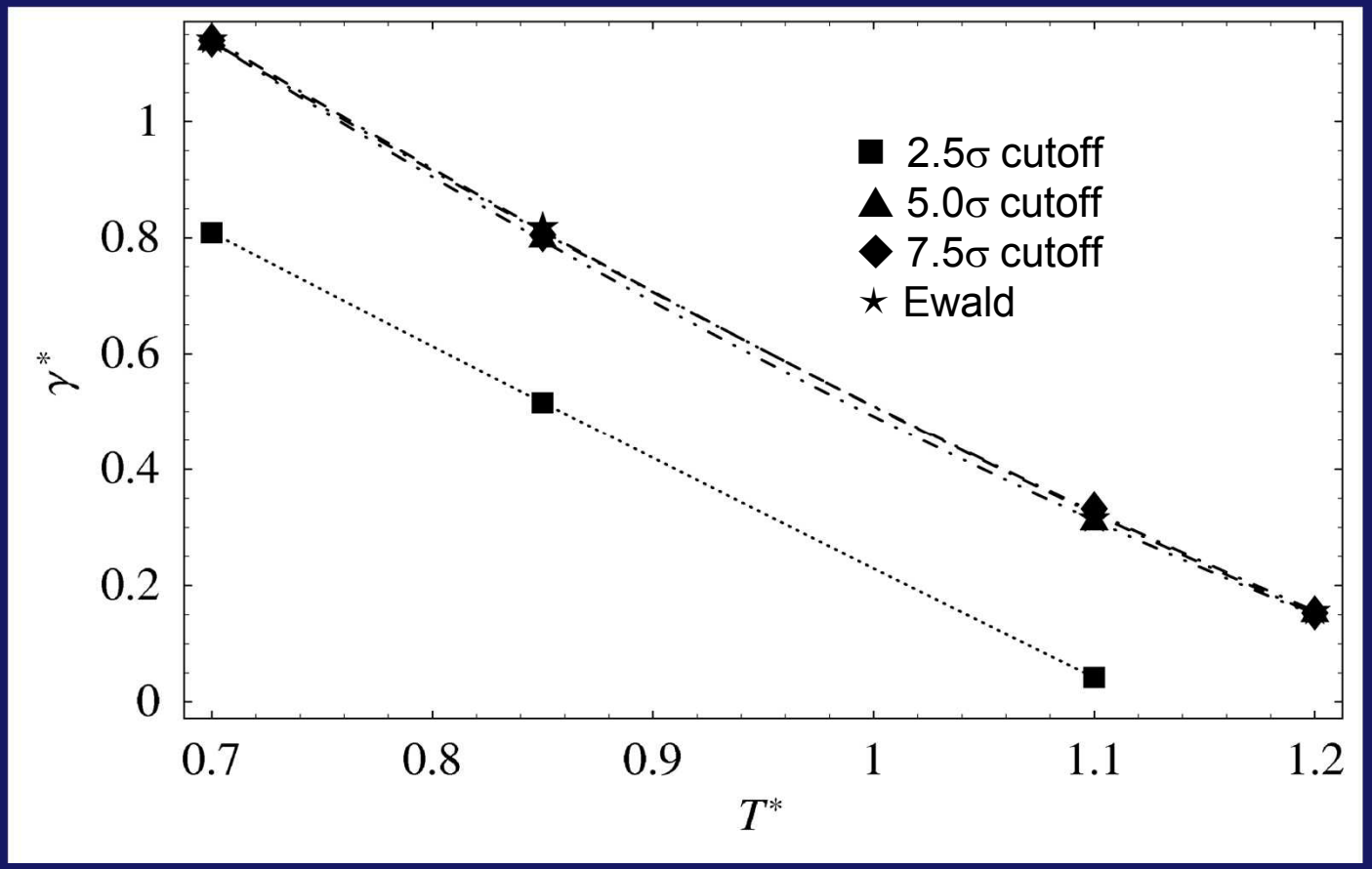
Lennard-Jones fluid: Surface tension



PPPM with ≥5σ cutoff needed to match Ewald results

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Lennard-Jones fluid: Performance

T^*	Method	r_c (σ)	Time per timestep (ms) $N_{particles} = 4000$ (4 procs)	Time per timestep (ms) $N_{particles} = 16000$ (8 procs)
0.70	Cutoff	2.5	5.2	18.4
	Cutoff	5.0	30.4	40.6
	Cutoff	7.5	98.7	135.0
	Ewald	5.0	95.1	124.6
0.85	Cutoff	2.5	5.4	6.7
	Cutoff	5.0	33.1	37.8
	Cutoff	7.5	115.1	129.0
	Ewald	5.0	87.7	121.9
1.10	Cutoff	2.5	3.5	6.4
	Cutoff	5.0	25.0	35.9
	Cutoff	7.5	76.2	119.7
	Ewald	5.0	67.3	103.5

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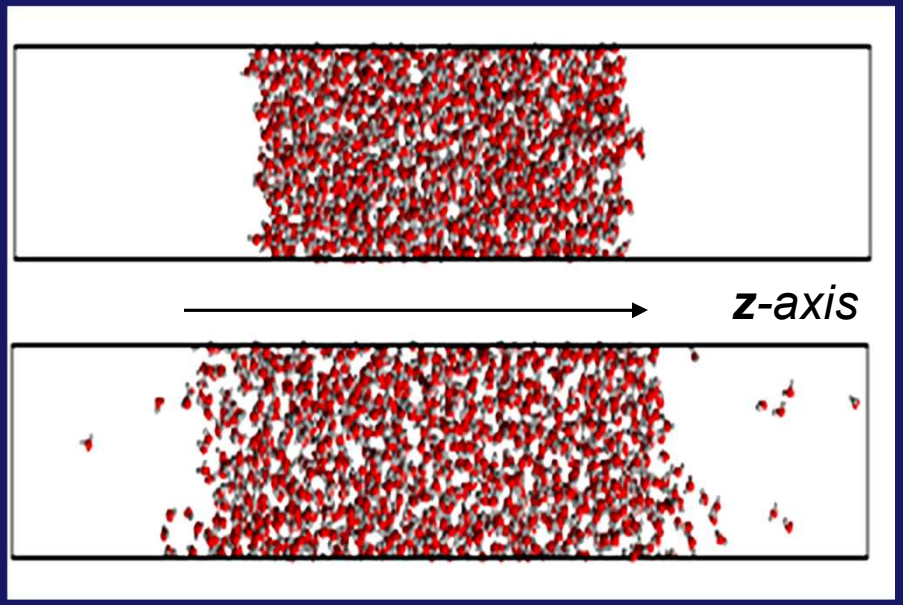
Water

Water slab at 300 K



Water slab at 500 K

- SPC/E water model
- 2200-10,000 molecules
- (36.5-77.4 Å)^2 x 150 Å box
- 10, 12, 16, or 20 Å cutoff for LJ dispersion; 10, 12, or 16 Å for Ewald summation
- 2 ns NVT MD simulations at 300 K or 400 K with 1 fs timesteps

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Water: Surface tension

Dispersion cutoff	$\gamma = \gamma_{sim} + \gamma_{tail}$ (mN/m)
10 Å	61.6
12 Å	61.7
16 Å	62.1
20 Å	61.3

Ewald "cutoff"	$\gamma = \gamma_{sim}$ (mN/m)
10 Å	61.8
12 Å	61.1
16 Å	60.5
Exptl.	71.7

Effect of long-range $1/r$ dominates $1/r^6$ contribution

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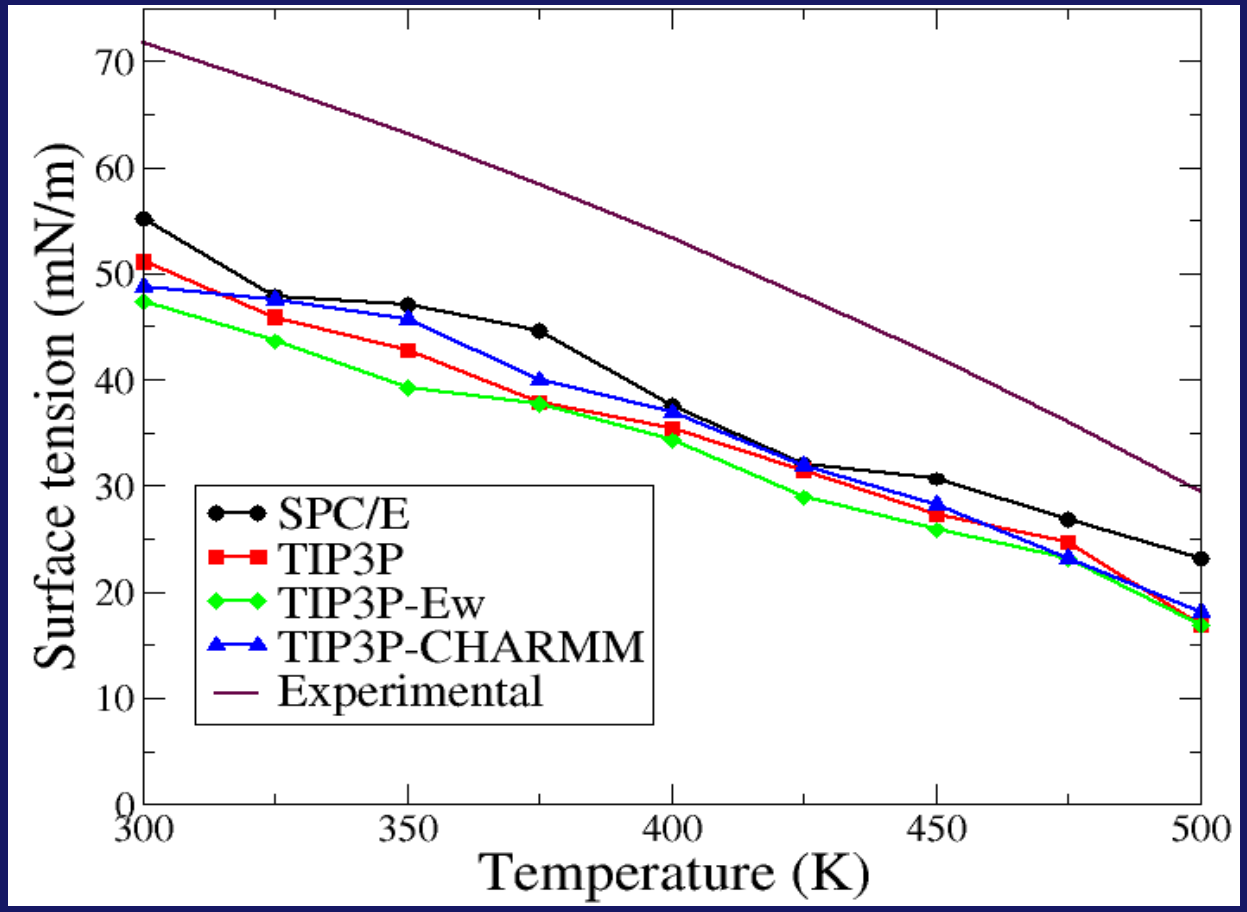
Surface tension of water



Disagreement with experiment a general feature of nonpolarizable models

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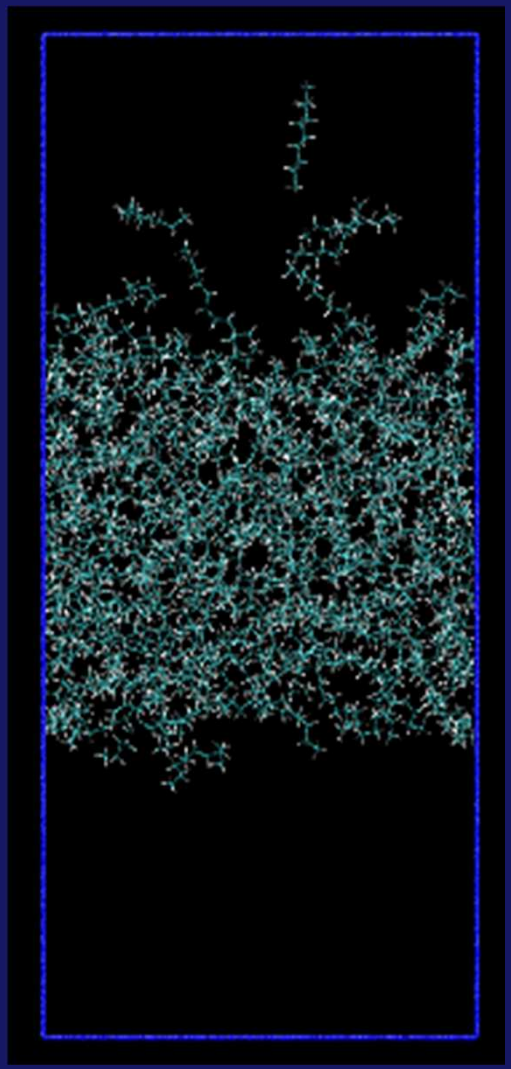
Alkanes



- C_6, C_{10}, C_{16}, C_{20}, and C_{48} chains
- Two all-atom force fields
  - OPLS: charges, LJ non-bonded
  - Smith et al. (2005): no charges, Buckingham non-bonded
- *NVT* simulations between 298 K and 550 K
- Time step 1 fs; simulations between 5 ns and 15 ns
- Long-range forces use PPPM with 12 Å or 16 Å cutoff or Ewald

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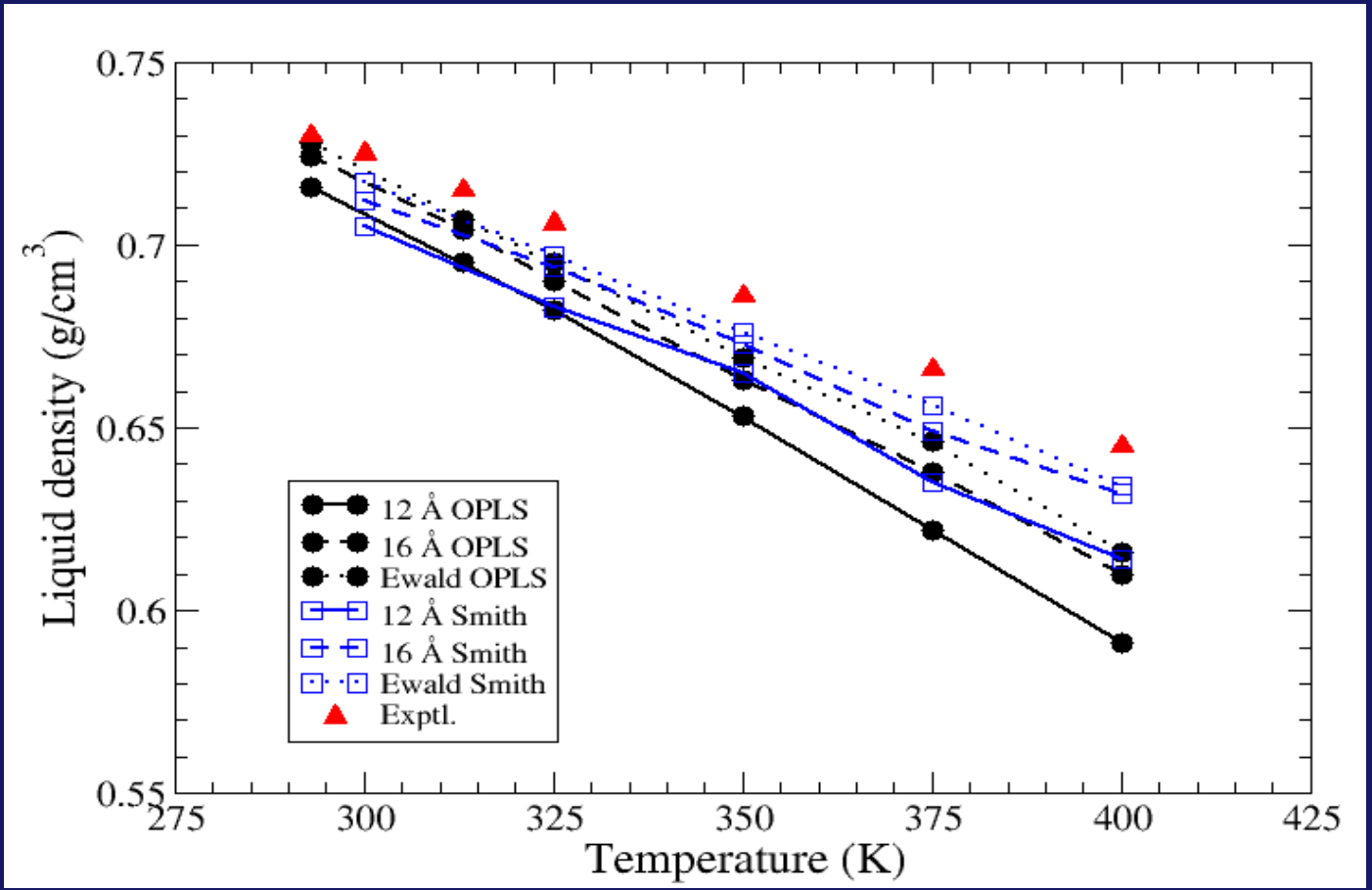
Alkane density



Ewald predicts density better than using large cutoffs

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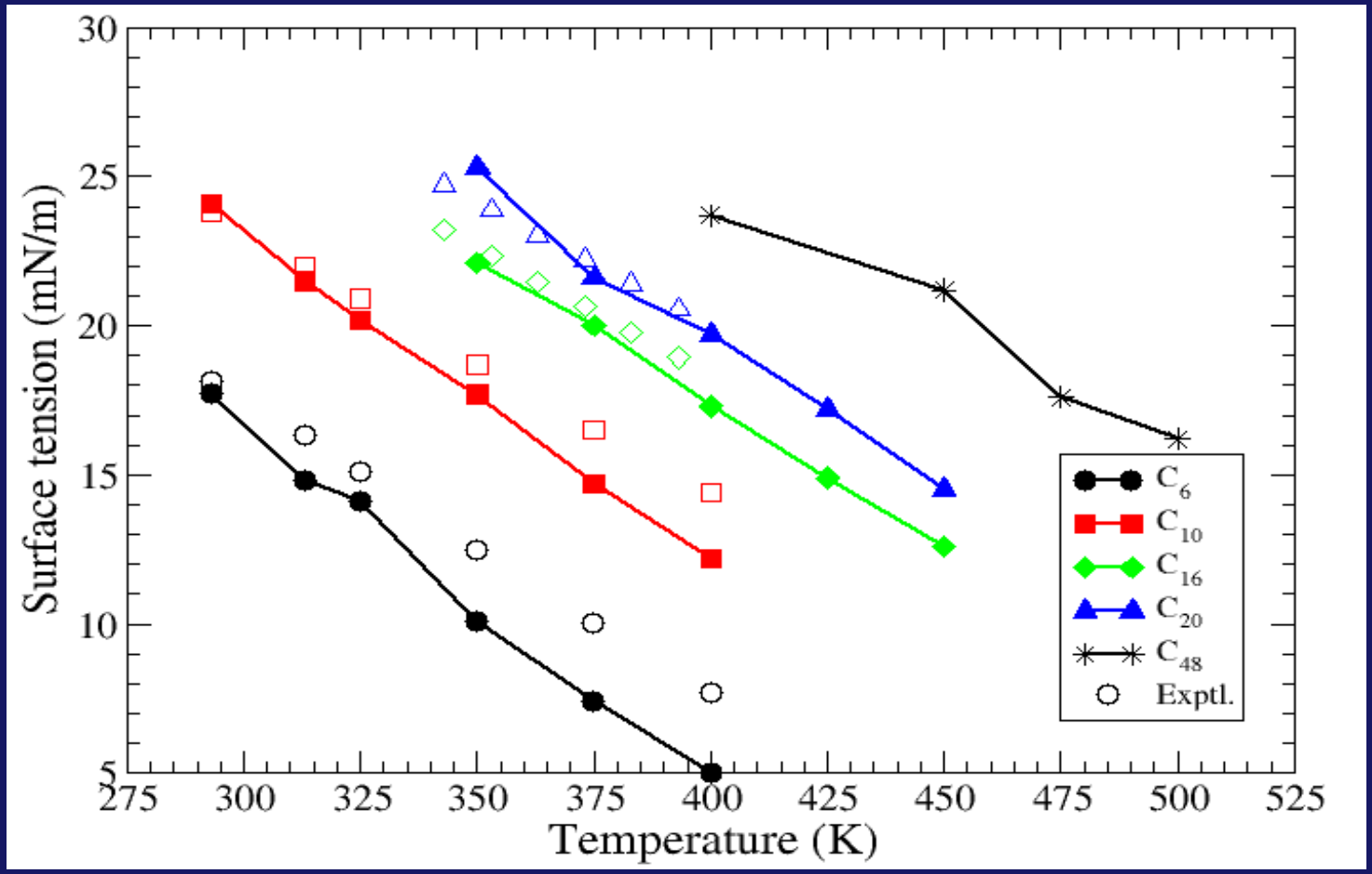
Alkane surface tension: OPLS FF



Good agreement at low temperatures using Ewald

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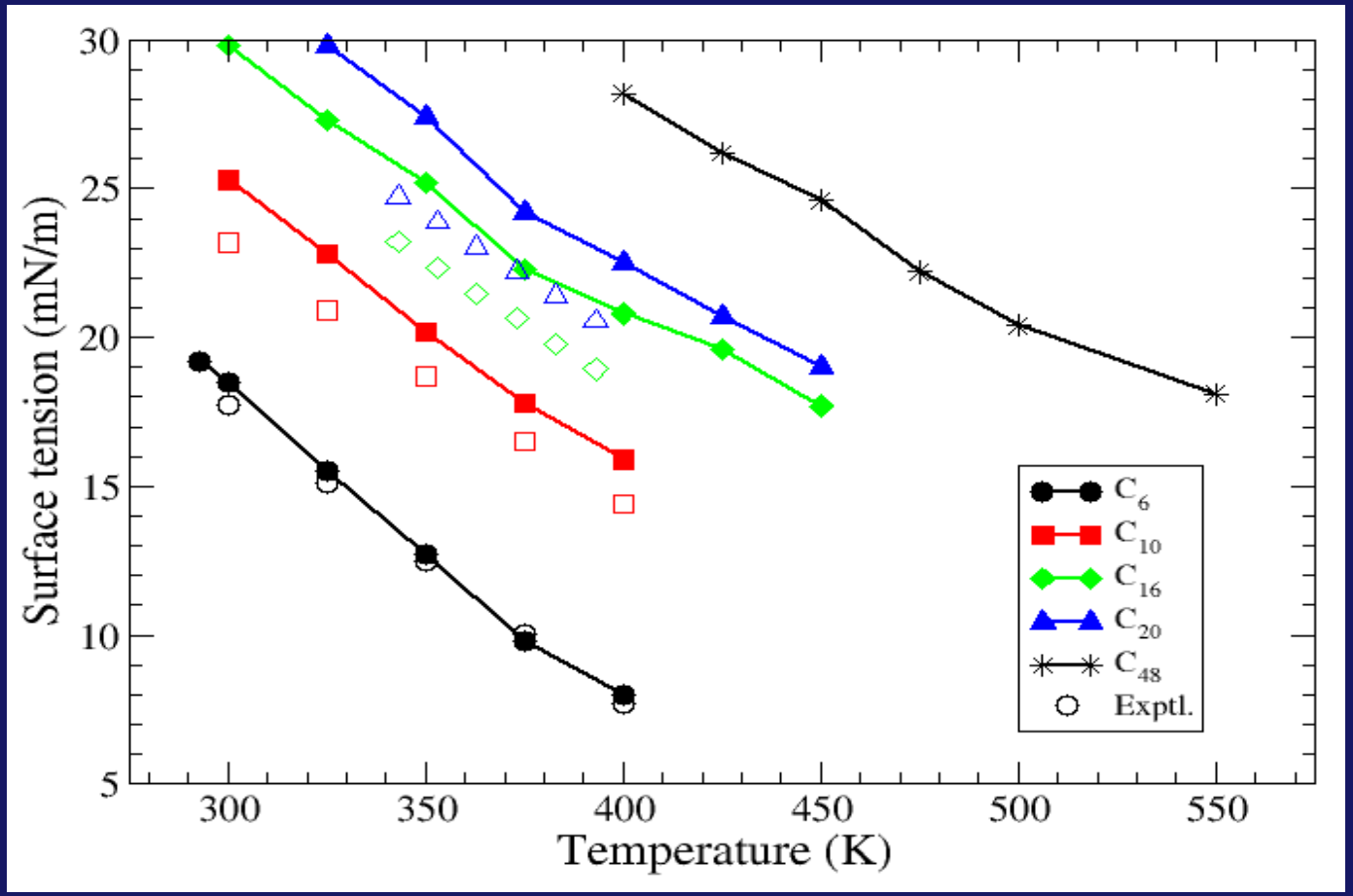
Alkane surface tension: Smith FF



Good agreement at low MWs using Ewald

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Conclusions

- Ewald summations of dispersion forces yield “true” results for a given pair potential
- The magnitude of long-range contributions increases with size of molecule
  - Increases need for long-range calculations
- Performance can be a factor, especially for dense systems
  - Is Ewald with a “moderate” cutoff better than brute force with a large cutoff?
  - Mesh-based implementations (PPPM, PME, etc.) can lead to improved speed without sacrificing accuracy

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