

Matching modeling and experiments
Teaching Demo - CMAT Soft Matter Modeling
Tenure-track position

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Learning outcomes

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- ▶ We will learn how to generate our own simulated data with molecular dynamics (constrained by available time)
- ▶ We will identify and discuss limitations of the computational models to fully reproduce the experimental reality and how to overcome them

Prior knowledge

- ▶ Basic thermodynamics: ideal gas law and virial expansion
- ▶ Basic molecular dynamics (can be introduced as part of this course)
- ▶ Basic ability to interact with a computer: simplified in this lecture; in the real course I would add a computer lab session.
- ▶ Prior programming experience can help the student delve deeper into the code and simulations, but is not required. Could be a special assignment/final project as part of the course.

Materials available online

All the materials (slides and codes) from this lecture are available at the course's online repository:

http://github.com/mcaroba/cmat_td

The equation of state of non-ideal gases

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Well-known ideal gas law

$$P = \frac{nRT}{V}, \quad P = \frac{Nk_B T}{V}, \quad R = k_B N_A \quad (1)$$

is only valid for low pressures and high temperatures. It neglects i) molecular size and ii) interatomic interactions.

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For real gases, we can use the virial expansion

$$P = k_B T \frac{N}{V} + B_2(T) k_B T \left(\frac{N}{V} \right)^2 + B_3(T) k_B T \left(\frac{N}{V} \right)^3 + \dots \quad (2)$$

In many cases of interest, $B_2(T)$ is enough to get a good description of typical gases at low T and/or high P .

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- ▶ We can accurately describe Ar at given conditions using the Lennard-Jones potential (pair-wise interaction potential):

$$V_{\text{LJ}}^{ij}(r_{ij}) = 4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right) \quad (3)$$

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ϵ_{ij} determines the energy scale ("strength") of the interaction between atoms i and j . σ_{ij} determines the length scale of the interaction: when it switches between strongly repulsive (at short range) and weakly attractive (at long range).

Connecting the equation of state with the interatomic interactions

For pair-wise potentials that only depend on the interatomic distance, $V(r)$, it can be shown¹ that $B_2(T)$ is a relatively simple integral of the potential:

$$B_2(T) = -2\pi \int_0^{\infty} dr r^2 \left(\exp \left(-\frac{V(r)}{k_B T} \right) \right). \quad (4)$$

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(we exploit the fact that $\lim_{r \rightarrow \infty} V_{\text{LJ}}(r) = 0$)

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Parametrizing a Lennard-Jones potential from experimental data

(in the real course, this would be done during a computer lab session in ~ 30 min.)

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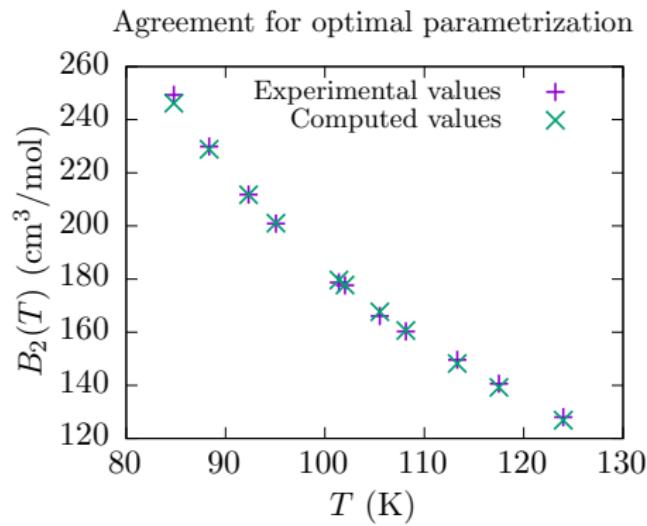
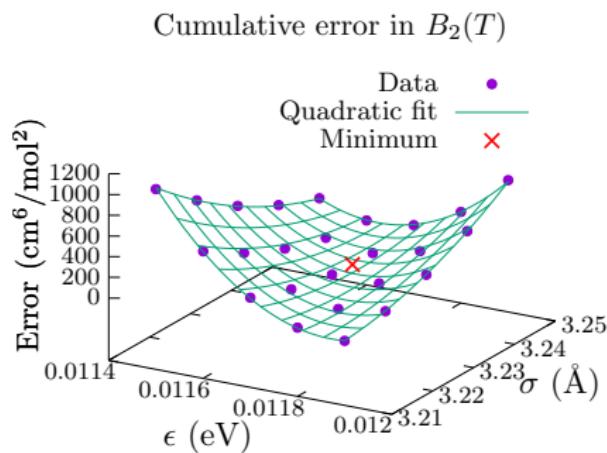
Let us take the following experimental data:¹

T (K)	$-B_2(T)$ (cm ³ /mole)
84.791	249.34
88.336	229.89
92.303	211.79
95.058	200.87
101.398	178.73
102.014	177.65
105.513	166.06
108.146	160.27
113.318	149.58
117.501	140.58
123.990	127.99

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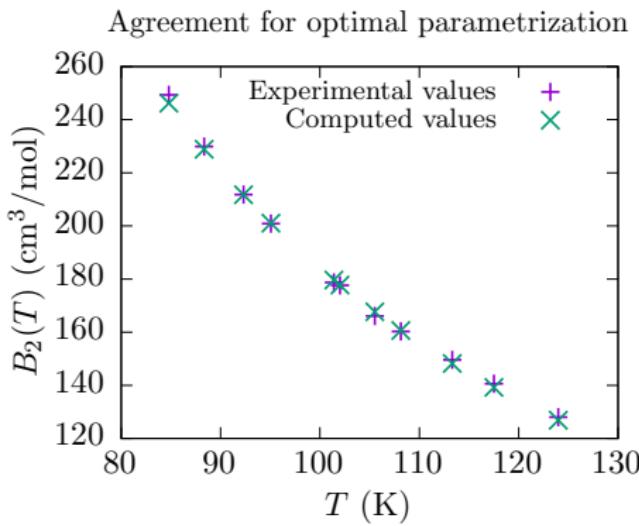
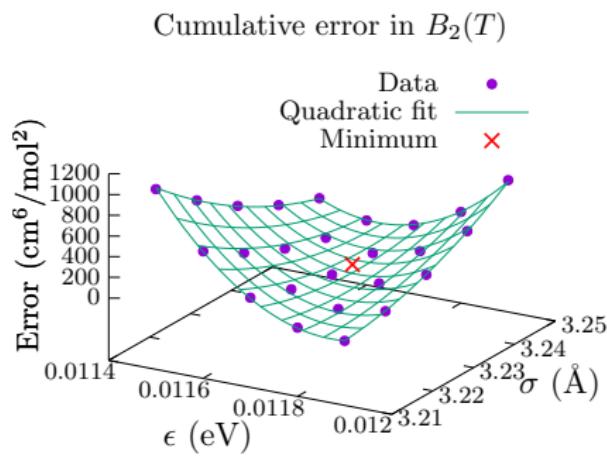
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where the error is defined as

$$\text{error}(\epsilon, \sigma) = \sum_i \left[B_2^{\text{LJ}}(T_i; \epsilon, \sigma) - B_2^{\text{exp}}(T_i) \right]^2. \quad (5)$$

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- ▶ We gather data points by changing the conditions between individual runs.
- ▶ For each run, we compute one P_i from that MD trajectory and then calculate one $B_2^i(T_i)$ from it:

$$B_2^i(T_i) = \frac{P_i - k_B T_i \frac{N_i}{V_i}}{k_B T_i \left(\frac{N_i}{V_i} \right)^2}. \quad (6)$$

Molecular dynamics (MD) simulation of argon at low temperature

Now go to:

<http://miguelcaro.org/lj>

(laptop and phone are both OK)

1) What is happening at low temperature?

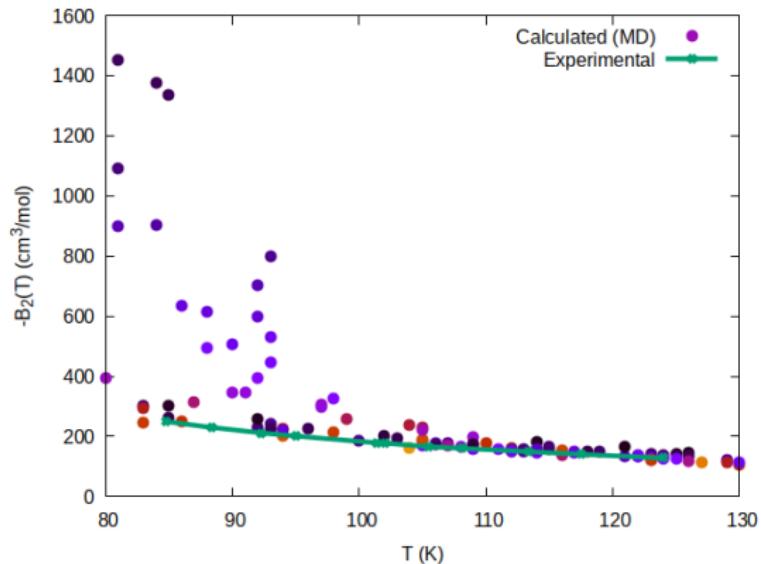
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The MD trajectories are not long enough to gather good statistics (due to time limitation of this lecture). How does it look like if you have more time?

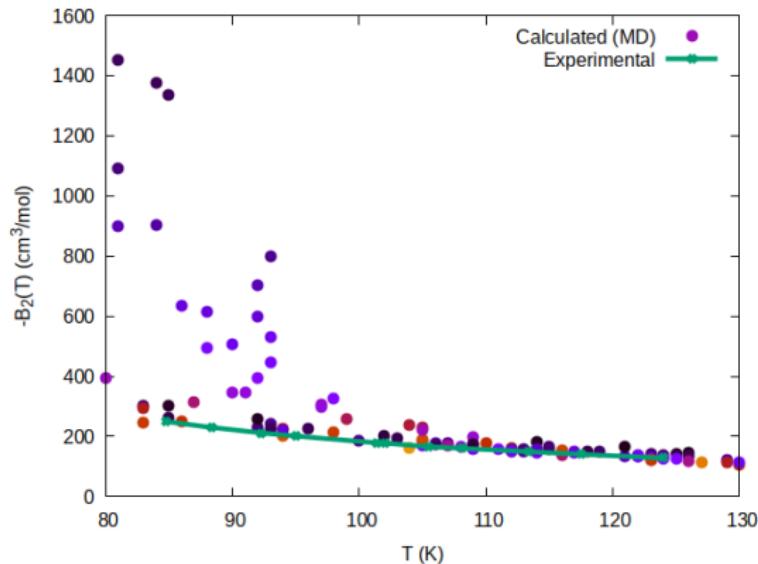
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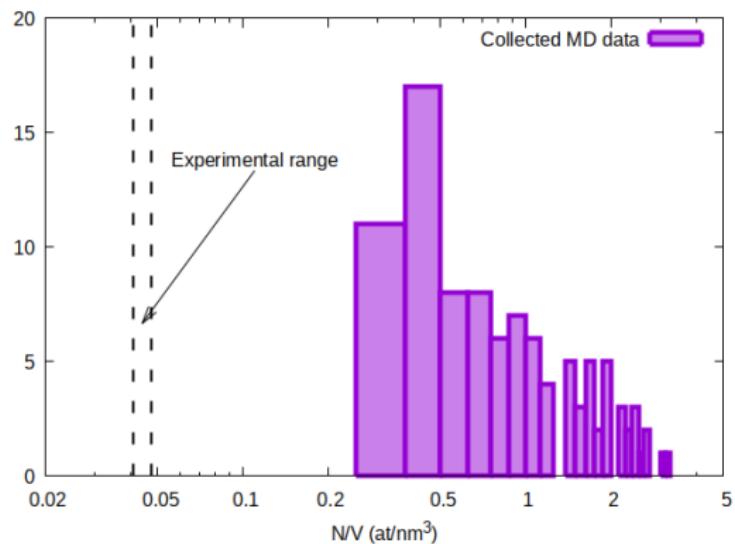
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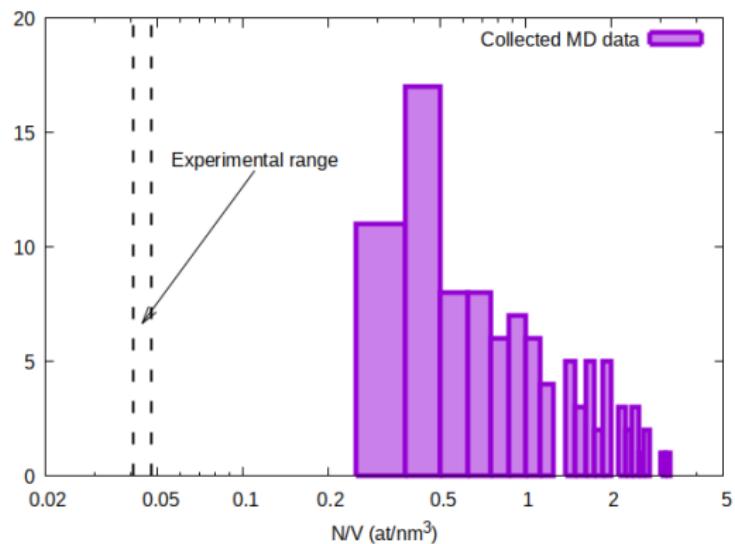
Keyword: **convergence**. Exercise: test convergence of $B_2(T)$ as a function of number of time steps used in MD.

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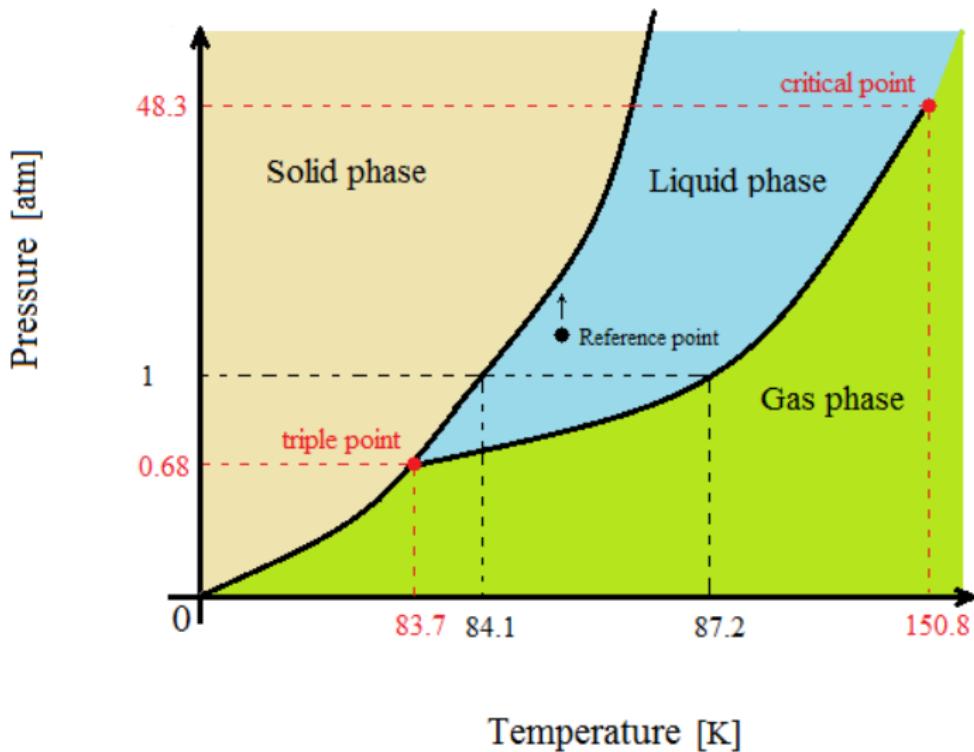


3) Even after convergence, at low temperature the simulation still does not match experiment! Why?



Due to our CPU constraints, we could not match the experimental conditions: very low density and long MD trajectories. The lower the density, the lower the chance for interaction between atoms; hence, even longer trajectories are needed to converge the results.

Experimental phase diagram of argon



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- ▶ To reproduce the experimental conditions as closely as possible: temperature, pressure, density, etc. Sometimes it is not possible due to computational constraints.
- ▶ Enough CPU to run the simulation.
- ▶ When the full experimental complexity cannot be reproduced (essentially, 100% of the time!), we can still get useful partial knowledge of the problem at hand.