Approaching the Marangoni Effect through equilibrium molecular dynamics

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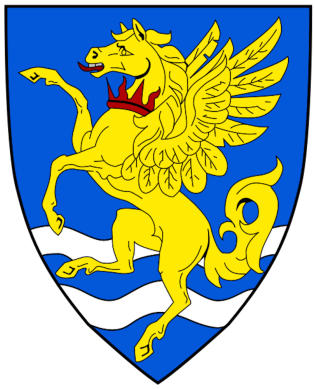

Acknowledgements

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Abstract

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Chapter 1

Introduction

The Marangoni effect is a liquid flow along a fluid-fluid interface as a result of either a chemical potential gradient or a temperature gradient tangential to the dividing surface. 2015 saw the 160^{th} anniversary of J. Thompson's first scientific investigation into this effect and yet whilst that period has seen a significant advance in our understanding of the phenomenom, a fully microscopic description evades us. Despite this, Marangoni flows are becoming ever more important with technological applications ranging from oil extraction deep within the Earth's crust to microfluidics on board satellites operating within low-gravity environments. This study will aim to simulate these flows as a result of a temperature gradient using a molecular dynamics simulation.

1.1 Early Studies

the "teardrops" that appear around the edge of a glass of wine provide the basis of the first study by J. Thompson into the Marangoni effect in 1855[?] . In this paper, Thompson describes how the preferential evaporation of alcohol from a thin layer of wine around the edge of the glass creates a more dilute liquid, which in turn generates a surface tension gradient. This gradient acts pull the wine in the bulk of the glass up the liquid-air interface and thus generates the flows observed within the glass. The phenomenom was later studied by Carlo Maragoni after whom it gets its name.

Since then, a number of studies have been made covering a wide range of manifestations of the effect from the formation of rings after the evaporation of coffee drops to the lateral transportation of microdroplets. Despite this large amount of research, the

1.2 Micro-gravity environments

In low gravity environments, thermocapillary becomes an incredibly important mechanism for fluid transport. On Earth, most fluid flow is driven by gravitational forces whilst in space, the low gravitational field causes surface driven effects to dominate. These surface forces may arise from capillary effects as well as thermocapillary forces and they ma Such flows are probably most commonly observed by the sharp-eyed wine connoisseur as teardrops forming along the edges of a wine glass just above the liquid surface, and this was the basis of the first study into the effect

Chapter 2

Molecular Dynamics

2.1 Estimating statistical error

With all experiments it is important to have a method of quantifying the statistical error in data, and computer simulations are not exempt. The measurements made in a molecular dynamics simulation are time-averages of observable and are evaluated over some finite simulation time as

$$A_\tau = \frac{1}{\tau}\int_{t=0}^{\tau} A(t)dt.$$

Frenkel and Smit show us that the variance in this average may be calculated as

$$\sigma^2(A) = \frac{1}{\tau^2}\int_0^\tau \int_0^\tau dtdt' \big\langle [A(t) - \langle A\rangle][A(t') - \langle A\rangle]\big\rangle$$

where the integrand is simply the time-correlation function of fluctations in A[?] . In the limit of a simulation time longer than the characteristic decay time t_A^c of the correlation function, this error reduces to

$$\sigma^2(A) \approx \frac{2t_A^c}{\tau}C_A(0).$$

This equation demonstrates to us the importance of accounting for correlation between data points in a molecular dynamics simulation. The ratio of $\frac{\tau}{t_A^c}$ gives the number of uncorrelated measurements, and thus it is clear that the variance is inversely proportional to this number. To estimate the statistical error, one needs only knowledge of the time correlation function

of the measured observable. However, calculating these functions induces significant computational cost.

Despite this, there exist methods for obtaining an estimate of the statistical error and an example of these is block-averaging. One particular method developed by Flybjerg and Peterson involves applying a blocking transformation to a data set to generate a new uncorrelated data set[?] . They show that the variance of an observable can be estimated as

$$\sigma^2(A) \geq \left\langle \frac{C_0}{n-1} \right\rangle$$

where C_0 is the value of the time-correlation function at $t = 0$ and is given by

$$C_0 \equiv \frac{1}{n} \sum_{k=1}^{n} (A_k - \bar{A})(A_k - \bar{A}).$$

The key to the analysis is to determine the value of this error by finding the block size at which this estimate reaches a plateau, thus providing a lower bound on the value of $\sigma^2(A)$.

Their method proceeds as follows:

1. Take a set of data $\{A_1, A_2, ..., A_n\}$.
2. Compute $\frac{C_0}{n-1}$ and use as an estimator for $\langle \frac{C_0}{n-1} \rangle$.
3. Apply the block transformation using $A'_i = \frac{1}{2}(A_{2i-1} + A_{2i})$. This halves the size of the data set.
4. Compute new estimate of error.
5. Repeat process until $n' = 2$.

   Using these data, it is then possible to plot the estimates for $\sigma^2(A)$ against the size of the individual blocks. In doing so, one can obtain a good estimate of the error from the value to which the data plateau. Their paper also provides an equation for estimating the error in $\sigma^2(A)$ which is independent of any assumptions; this is given as

$$\sqrt{\frac{2}{n-1} \times \frac{C'_0}{n'-1}}.$$

They note that this method gives the same statistical error as the more theoretically rigorous time-correlation method but with a dramatic decrease in computational cost.

Using a standard binary mixture simulation identical to those used to calculate the Marangoni forces at the interface, a blocking analysis was carried out for a simulation time of 10^6 timesteps and 10^7 timesteps as shown in Fig 2.1. These data show a clear plateau at a block size of 10,000 timesteps for the longer simulation time and 5,000 timesteps for the shorter run, with little increase in the error of σ^2 until a much larger block size. This information can be used to infer a suitable size for block averaging data within a LAMMPS simulation in order to yield sufficient decorrelation of individual samples and a good estimate of the statistical error.

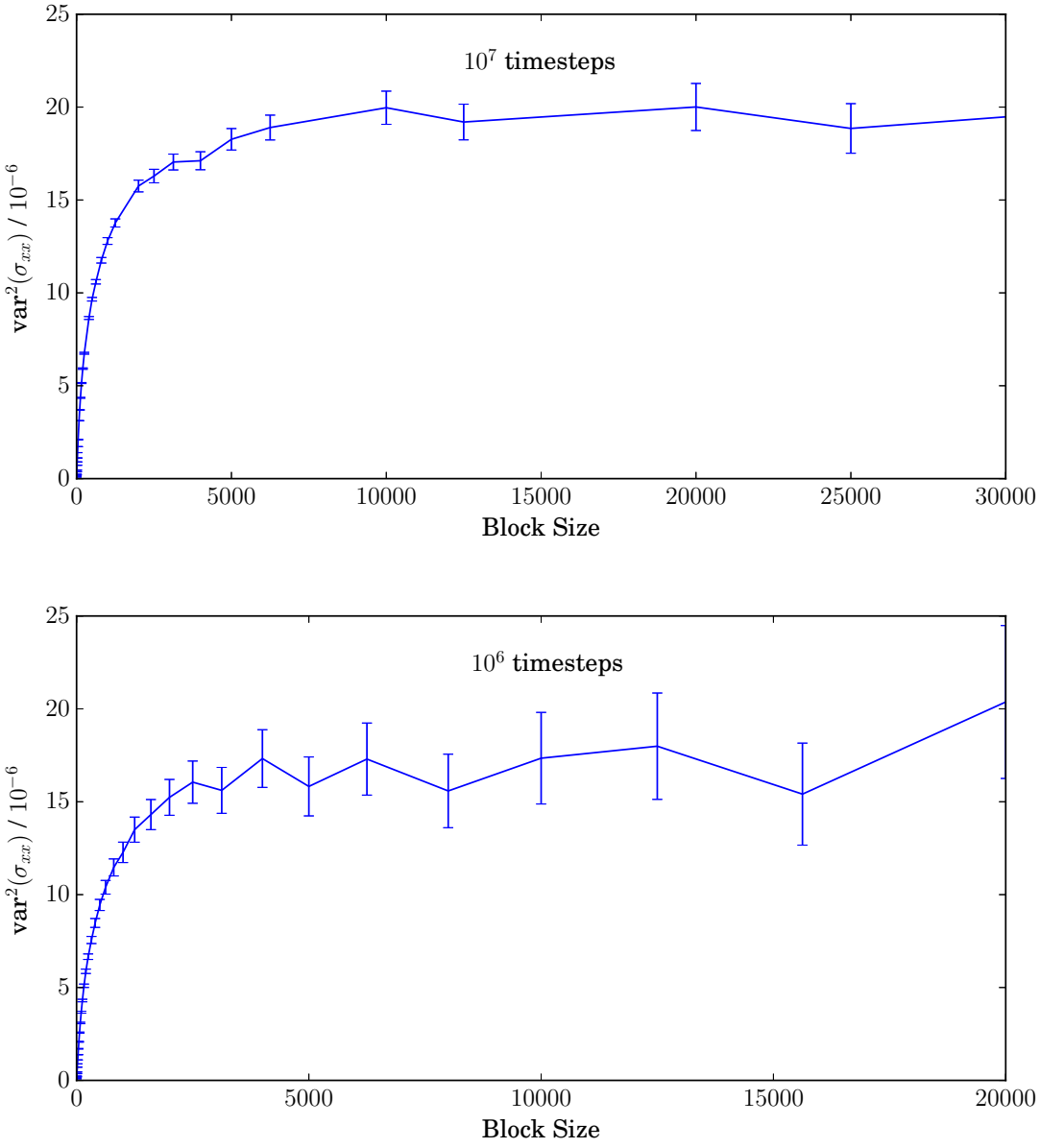

Figure 2.1: The blocking analysis for a simulation time of 10,000,000 timesteps and 1,000,000 timesteps shows clear plateaus in the estimate of the error at block sizes of 10,000 and 5,000 respectively. This can be used to estimate the size of blocking needed to decorrelate data in the correspinding molecular dynamics simulations.