Draft for the thesis

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Summary Document for the draft of the Thesis.

Introduction

Molecular Dynamics

[1]

[1]

- Lagevin thermostat
- Brownian Dynamics

Virial Stress and Cauchy stress

Main articles for this section:

- On mechanical theorem application to heat
- The virial theorem and stress calculation in molecular dynamics
- General formulation of pressure and stress tensor for arbitrary many-body interaction potentials under periodic boundary conditions

The virial stress developed on the virial theorem of Clausis 1870 and Maxwell 1870 is

$$\sigma_{ij}^{V} = \frac{1}{V}\sum_{\alpha}\left[\frac{1}{2}\sum_{\beta=1}^{N}\left(R_i^{\beta} - R_i^{\alpha}\right)F_j^{\alpha\beta} - m^{\alpha}v_i^{\alpha}v_j^{\alpha}\right], \tag{1}$$

where (i, j) represents the directions x, y and z. β goes from 1 to N representing the neighbors of the particle with index α. Therefore, R_i^{α} is the position of the particle $alpha$ along the direction i, meanwhile $F_j^{\alpha\beta}$ is the force on particle α due to the interaction with particle β in the j direction. Finally, V is the total vovlume of the system, m^{α} is the mass of the particle α and v_i^{α} is the velocity of the particle α in direction i. It is important to acknowledge that the force $F_j^{\alpha\beta}$ is uniquely defined only for pair potentials and EAM type potentials.[2]

[2] So. . . I need to check[Swenson, 1983] and[Tsai, 1979] to understand how we get that expression from the virial theorem. Also, I don't know what is the virial theorem

The virial stress calculated from molecular dynamics (MD) simulations has to be averaged voer time in order for it to be equivalent to the continuum Cauchy stress[Subramaniyan and Sun, 2008].

Viriral stress is indeed an atomistic definition for stress that is equivalent to the continuum Cauchy stress.

Molecular dynamics simulations are typically performed in the Eulerian reference frame[3] and hence will need to have velocity included in the stress definition.

[3] I don't know what is the defference between the Langrangian framework and the Eulerian reference frame.

Pressure and stress relation

Pressure and stress are familiar physicla notions. Both refer to the force per unit area which two bodies in contact, or two parts of a single body separated by an imaginary plane, exert on one another. Both tensorial quantities[Tsai, 1979]. Under hydrostatic conditions, the relationship between external pressure and internal stress is particurlarly simple:

$$P = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}), \tag{2}$$

where $\sigma_{xx} = \sigma_{yy} = \sigma_{zz}$ and $\sigma_{xy} = \sigma_{yz} = \sigma_{zx} = 0$, that is, at equilibirum, the external pressure P is equal to the internal normal stress components and throught the system, the shear components being zero. Under these conditions, the external pressure may be calculated from the virial theorem:

$$PV = NkT - \frac{1}{3}\left\langle \sum_{i,j<1}^{N} \vec{r}_{ij} \cdot \frac{\partial \Phi_{ij}}{\partial r_{ij}} \right\rangle, \tag{3}$$

where V is the volume, N is the number of particles, T is the tmeperature of the system, k is the Boltzmann's constante, r_{ij} is the vector joining particles i and j and Φ_{ij} is the interatomic potential between i and j. The angular brackets denote average over time[4].

[4] Is the same expression for the scalar pressure used by the compute pressure in lammps: documentation page.

The instantaneous internal stress ar a point is made up of two parts:

- The sum of the interatomic forces intercepted by a small area containing the point, averaged over the area.
- The momentum flux through this area during a time interval Δt

If an atom moves across the area, carrying momentum Δmv, then the area also "feels" a force equal to the momentum flux $\Delta mv/\Delta t$, and the force also contributes to the stress over the area in the interval Δt. The normal component of the sum of the forces gives the normal stress, and the in-plane component gives the tangential stress. The area may be either stationary or moving at a uniform velocity. It may also be at the boundary of the system.

The time averages of the instantaneous stress components then ive what may be called the "measured" stresses at the point.[Tsai, 1979]. ... This formulation is not new: Cauchy discussed the stress-strain relationship in a crystalline material from the viewpoint of "region of molecular activity" as early as 1828. ... The stress method applies equally to a system not in thermal equilibrium, because the temperature term does not appear explicitly in this formulation. ... the method of stress calculation may be applied locally, without requiring the system to be in equilibrium or even spatially homogeneous. ... it should be possible to use this method to obtain the stress distribution in a solid with a crack in it, whereas the virial method would be inapplicable in this case.

They show that the pressure calculated by the vrial method is actually the normal stress in the boundary planes. The stress method, on the other hand, can be used to calculated the stress not only in the boundary planes, but also in the interior planes.

The virial is defined as

$$\Upsilon = \sum_{i}^{N} \vec{r} \cdot \vec{F}_i, \tag{4}$$

Lammps implementation

Langevin Thermostat

compute stress/atom and pressure [5]

Virial contribution to the stress and pressure tensors[Thompson et al., 2009]. They find three ways of computing the virial contribution,

$$W(\vec{r}^N) = \sum_{k\in\vec{0}} \sum_{w=1}^{N_k} \vec{r}_w^k \cdot \vec{F}_w^k \tag{5}$$

$$W(\vec{r}^N) = \sum_{n\in Z^3} \sum_{i=1}^{N} \vec{r}_{i\vec{n}} \cdot \left(- \sum_{k\in\vec{0}} \frac{\mathrm{d}}{\mathrm{d}\vec{r}_{i\vec{n}}} u_k\left(\vec{r}^{N_k}\right) \right) \tag{6}$$

$$W(\vec{r}^N) = \sum_{n\in Z^3} \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i + \sum_{\vec{n}\in Z^3} \mathrm{Hn} \cdot \sum_{i=1}^{N} \left(- \sum_{k\in\vec{0}} \frac{\mathrm{d}}{\mathrm{d}\vec{r}_{i\vec{n}}} u_k\left(\vec{r}^{N_k}\right) \right) \tag{7}$$

6

[5] Explain the scalar pressure, pressure tensor and stress tensor. Explain the relation between pressure and stress of the system.

[6] Skimming the equations (1) and that one, the virial term are similars. Need to check if they are equivalents.

Stress

Stress is an important concept in characterizong the states of condensed matter. A body is in a state of stress if it is acted upon by external dorcer or, more generally, if one part of the body exerts forces upon another part. If we consider a volume element within a stressed body, we can distinguish the effect of two types of forces: those acting directly in the interior of the elemnt and those exerted upon the surface of the element by the surrounding material. The latter forces (per unit area) are stress that are transmitted throught the interior of the volume. For condensed matter in which the stress is homogeneous in volumes of macroscopic dimensions, the equation of state in the relation between the stress and the internal variables, such as the density and temperature.[7]

In order to describe general flow gradients, the velocity gradient tensor, the deformation tensor and the stress tensor are mathematical entities that help in doing so. The velocity gradient tensor describes the steepness of velocity variation as one moves from point to point in any direction in the flow at a given instant in time. The deformation gradient tensor describe the deformation history in a complex fluid. Lastly, the stress tensor represent the force per unit area that is exert on a surface.[8]

In general the stress tensor is modeled with two terms,

$$\mathbf{T} = \text{\textbf{œ}} - p\,\text{\textbf{ffi}}. \tag{8}$$

where **œ** represent the stress tensor related to internal phenomena of the system and the second term consider external pressure to the system, more specifically, the atmospheric pressure. …since we are interested in the response of the material our analysis will be center in **œ** …To do it so, we analyze the virial stress to find the macroscopic (contoniuum) stress, because we are going to use molecular dynamics computations[9]. The macroscopic stress tensor in a macroscopically small volume Ω is typically taken to be:

$$\sigma_{\alpha\beta} = \frac{1}{\Omega} \sum_{i\in\Omega} \left(\frac{1}{2} \sum_j \left(x_\alpha^{(j)} - x_\alpha^{(i)} \right) f_\beta^{(ij)} - m^{(i)} \left(u_\alpha^{(i)} - \bar{u}_\alpha \right) \left(u_\beta^{(i)} - \bar{u}_\beta \right) \right) \tag{9}$$

where… α, β are x, y, z.… …to reduce random fluctuations (because we are using Brownian dynamics) we perfom a spatial and time average. The

[7] Cite Quantum-mechanical theory of stress and force

[8] Cite Larson Book Introduction to Complex Fluids

[9] Cite Physical Interpretation of the virial stress

$1/\Omega$ factor is due to the spatial average, meanwhile the time average are the terms in equation (9). The first term emerges from the virial theorem of Clasius, and the second term is a correction ter that emerges from the "cross-over" phenomena, when analyzing at microscopic scale.[10]

[10] Explain more

References

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