Control Volume Formulation Applied to Molecular Dynamics

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Outline

. Introduction

- Continuum Mechanics
- Molecular Dynamics
- . Irving and Kirkwood (1950) and the Dirac delta

. The Molecular Control Volume

- . The Control Volume function
- . Governing equations
- Exact conservation

. Applications

- . The pressure tensor
- . Unsteady Couette flow
- Coupled simulations and constrained dynamics

Introduction



Continuum vs. Discrete

. Assumed Continuous at every point in space

. Mass Conservation

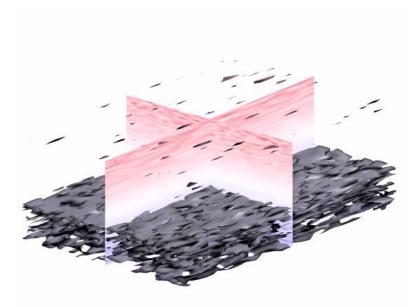
$$\frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla} \cdot \rho \boldsymbol{u}$$

. Momentum Balance (Newton's Law)

$$rac{\partial}{\partial t}
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abla} \cdot
ho oldsymbol{u} oldsymbol{u} = oldsymbol{
abla} \cdot oldsymbol{\Pi}$$

. Energy Conservation

$$\frac{\partial}{\partial t}\rho \mathcal{E}dV = -\boldsymbol{\nabla}\cdot \left[\rho \mathcal{E}\boldsymbol{u} + \boldsymbol{\Pi}\cdot\boldsymbol{u} + \boldsymbol{q}\right]$$



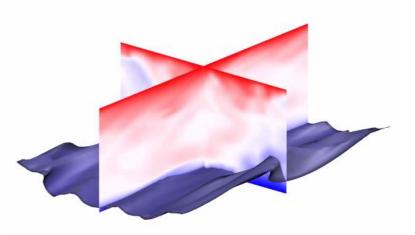
Direct Numerical Simulation of Turbulent Couette Flow

Continuum vs. Discrete

. Discrete Molecules in continuous space

- Governed by Newton's Law for an N-body system
- . Point particles with pairwise interactions

$$m_i \ddot{\boldsymbol{r}}_i = \mathbf{F}_i = \sum_{i \neq j}^N \boldsymbol{f}_{ij}$$
 $\Phi(r_{ij}) = 4\epsilon \left[\left(\frac{\ell}{r_{ij}} \right)^{12} - \left(\frac{\ell}{r_{ij}} \right)^6 \right]$



- How do we obtain equivalent descriptions?
 - Both modelled by Newtonian mechanics
 - Linking the discrete and continuous forms

Molecular Dynamics Simulation of Couette Flow

Imperial College London

(2.3) for the probability distribution in Gross phase space and then perious repealed laterations. Since * This work was supported by the L.S. ONR under Oxtract Ninart 24 with the California Indirect of Twelmenby, J. G. Kirkwood, J. Chem. Phys. 14, 30 (1946)

more that the activity and current activity in the configuration space of a pair of molecular. The re-sults were resolved to show the fact activity of acthe contiguration space of a pair of non-enders. The re-sults were previously stated in the first article of this arties, when this definition was promited. To obtain explicit expressions for the pair probability density and revealability expressions denotes are sensed to To obtain explicit expressions for the pair probability density and probability current density one would in principle need to police the Linuville equation [Eq. (2.3)] for the grobability distribution in Gives phase over a data then readous constant terministic Since

THIS paper will be concerned with a derivation of the equations of hydrodynamics from the mini-His paper will be concered with a derivation of the espations of hydrodynamics frem the cipies of the classical statistical mechanics. In pargeneralization of the well-known rocker-rance coun-tion of stochastic theory, has been derived by Kjrk-100 U STOCHASTIC ID0075, DAS UPEN DETVOU DY ANTA-10000 hy introducing the concepts of time smoothing and a faction concepts of the terms concepts has been ciples of the classical statistical mechanics, in par-ticular, the equation of continuity, the equador of motion, and the equation of energy transport will be wood ny introducing use concepts as true smoothing and a triction constant. This latter equation has been and a triction constant. Loss after equation has occar applied to obtain an expression for the stress tensor notion, and the equation of energy transport will be derived. By so doing, the stress tensor and heat current derived and be an energy of the stress tensor and tenso derived. If so doing, the stress tensor and boll current density can be expressed in terms of molecular variables. The stress service consists of a location of the location density can be expressed in terms of molecular variables. The stress tensor consists of a kinetic part (which excurs in the kinetic fueror) of gaugi and another term (dominant for a liquid) which will be expressed as a modering involving the constraint of intermetation trommant for a neuron will be expressed as a quadrature involving the potential of intermulecular force and the second of ratio of evolution of the last quadrature involving the potential of intermalecular force and the viewity of pairs of molecules. The best force and the uensity of pairs of molecules. The best current density is the sum of the ismiliar kinetic part current density is the arm of the forminar unger par-and a quarketure involving the potential of inter-noicentar force and the density and current density and the content of the density and current density and the content of the density of currents are the second

approximately by the probability distribution function in the phase space of a rair of molecules. One such equa-tion has been derived by Born and Green' using a rescalined "superposition" assumption. Another, a superposition of the next process pathware built. reacting aperiositica assumption. Another, generalization of the well-known Fokker-Planck equi-

have been made to obtain a closed equation satisfied approximately by the probability distribution function

The equations of hydrolynamics—conticulty equation, equation of easier, and repeations of energy tradpert- are derive with beam as at the classic contribution mechanics. Thereby, oppeadicular to the familiar for the system tensor with one accurate device in terms of underived results, and and the system tensor is an energy of the system are across depending yours expression, respectively are accurate in terms of the system are across depending yours expression, respectively and the system in terms of the system are across depending your expression, respectively and the system in terms of the density tend currents, density in the configuration space of a pair of underside, as quadratures of the density tend currents, density in the configuration space of a pair of underside. this program is untenable for a liquid, various attempts une program se untenance sor a numa, vanous autorana have been unde to obtain a closed equation satisfied

The Statistical Mechanical Theory of Transport Processes. IV. The Equations of Hydrodynamics* J. H. IRVING AND JUNY G. EUROWOOD Gates and Crelline Jahrmieries of Chemistry No. 1343, Passdene, California (Resoluted Konsender 31, 1963).

Jerome Karle lot electron diffraction dats; and to Dr. E. K. Phyler and the National Bureau of Standards for lata in the long wave-kngth region. 210+558 cm⁻¹. The faint sharp Raman band at 835. cm⁻¹ has been interpreted as an upper-stage band. 2X a07 + v₀ − v₀, rabter than as the R₂, difference band 1540-510 cm⁻¹, because the corresponding sum band VULUME 15. NUMBER 6 THE INCREAT OF CREMICAL PHYSICS

175.9 cm⁻¹. The band at 809.7 cm⁻¹ has been interpreted 17: 9 cm⁻⁴. The band at 300.7 cm⁻¹ has been interpreted as 22×394, the rather large difference between calculated and decoursed forements being standard to the communic is $3X_334$, the rather large difference between calculated and observed incomency being a scriber, to the "proximity to the A_2 (undermand). However, this hand could be an unstationer band commenceding to Stutement to the A_s (undamental. However, this band could be an upper-stage band corresponding to 819 cm⁻¹. The interpretation of the faint sharp lund at 769.4 cm⁻¹ as an upper-stage band, $778 + \nu_{err} = n$ genus more blushle than its interpretation as the B_{ν} combination. cm⁻⁻ as an upper-stage band, $778+e_{1}-e_{2}$, seems more plausible than its interpretation as the B_{12} combinition 3101-552 cm⁻¹. The first show the second local second plausible than its interpretation as the H w consummation, 2104-558 cm⁻¹. The faint sharp Raman band at \$28.5 methods been been been under the unmanifold processing band

and 8.50 cm⁻¹, are related to each other in much the same manner as similar groups in the spectra of CO₂ and CS₂. The writers wish to express their inceptedness to Dr. The writers wan to express their incediedness to Dr. C. F. Hanmer and E. L can point de Nemours and C. F. Hammer and E. L Gu Pont de Nemours and Company for the samples; to Doctors Isabella and Jerone Karle for electron diffraction data; and to Dr. F. K. Budes and the Network Decomposition of Complete Long

TRANSPORT PROCESSES

has not been observed. If the preferred interpretations this hot been ouserved, it the preferren interpretations are correct, the group of Raman hands, 769, 778, 819, and 829 cm², are related to each other in much the same

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applied to obtain an expression for the stress innor-linear in gradierts of third velocity and, thereby, ex-

linear in granteris of fluid velocity and, incessivy, ex-pressions (in terms of molerular variables) (or co-efficients of abeat and volume viscosity.) The same

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atter uneariang in the temperature grausers, sens to an explicit expression for the hear current and thereby

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ducibyly. We shall assume, for purposes of malle-natical simplicity, a single component, single place duid content conductor of molecular uplich interact

CallCal simplicity, a single component, angle page fuld system consisting ul nolecules which interact under central forces only. It is not difficult to generalize the treatment to a multicle common to emultice

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M. USAMMAN, M. S. Creen, Proc. Roy, Suc. A188, 10 (1996). N. Boen and M. S. Creen, Proc. Roy, Suc. A188, 103 (1987). N. Elbanovol, Starkan J. Chem. J. Chem. The strain widel weather than the strain and the strain and the strain widel weather than the strain and president composation of up the effect instal disciplination function.

pressure for the cochostic of method cor-

Irving and Kirkwood (1950)

561-10 The probability distribution function (relative den-as the expectation value of the dynamical variable sity of representative points in phase space) we denote $d' \int \mathcal{E}_{R}$ satisfying the normalize tion condition $\int \cdots \int f d\mathbf{R}_{i} \cdots d\mathbf{R}_{i} c \hat{q}_{p_{i}} \cdots dp_{n'=1}$ (2.1)

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Thus, (2.4) becomes

where $d\mathbf{R}_{4}$ stands for a volume element π the con-summation more and d_{2n} is volume element in the more where $d\mathbf{R}_{t}$ stands for a volume element in the con-figuration space and $d\mathbf{p}_{t}$ a volume element in the mo-mentum space of the 4th molecule, stands in the mo-security of the society of the standard in the security of the sec mentum space of the still molecule. ; Charges 1 according to the well-known Liouville equation

 $\frac{df}{dt} = \sum_{k=0}^{N} \left[-\frac{p_k}{m_k} \nabla \mathbf{R}_k f + \nabla \mathbf{R}_k U \cdot \nabla \mathbf{P}_k f \right]$

where U is the potential energy of the entire system. Any cynamical variable, $\alpha(\mathbf{R}_1, \dots, \mathbf{R}_n; \mathbf{R}_n; \mathbf{n}_1, \dots, \mathbf{R}_n)$, bas an expectation value given at time / by

 $\langle \alpha_{i,j} \rangle = \int \cdots \int \alpha \langle \mathbf{R}_{l_{1}} \cdots \langle \mathbf{p}_{l_{l}} \cdots \rangle / \langle \mathbf{R}_{n} \cdots \langle \mathbf{p}_{u} \cdots \langle l \rangle$

If the array We thus denote he (a; f) the expectation value of a that the kth in induct of a and j taken over the smartly the inner $\left(\partial(\mathbf{R}_{i} - \mathbf{y}_{i}) \right)^{n}$. Froughing a does not decord on time employible the f

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+ (a; VesU-Vost) . (2.4)

Providing a cose not depend on time explositly, the rate of change of the expectation value of a is given by

 $\frac{\partial}{\partial t}(\alpha_i, f) = \left(\alpha_i, \frac{\partial f}{\partial t}\right) = \sum_{k=1}^{N} \left[\left(\alpha_i, \frac{\mathbf{p}_k}{\mathbf{m}_k}\right) - \frac{\mathbf{p}_k}{\mathbf{m}_k} \right]$

By Green's theorem applied in the space of Ra

providing the integrated part vanishes; i.e., providing the system is bounded or f falls off sufficiently applied as R. I. I. Kenning simo up, f is independent of applied

the gystem x bounded or f tails of sufficiently tags as $R_{k} \rightarrow \infty$. Likewise, since $\nabla R_k f$ is independent of mentum n, and since f is in or satisfies as a second

is $K_{k} \to \infty$. Likewise, since V_{k+1} is unependent meature p_{k} and since f falls off rapidly is period.

of Green's theorem in the momentum space of g

 $(\alpha; \nabla R_k U \cdot \nabla p_k f) = -\langle \nabla R_k U \cdot \nabla p_k \alpha; f \rangle$

 $\rho(\mathbf{r},t) =$

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 $S(x_n)f(x,y)dy = f(x,y)?$

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Sol The TRACE VEGUE POR We shall use (2.7) to derive the equations of hydro- Avnomize

III. STATISTICAL MICHANICAL EXPRESSIONS FOR DENSITIES

 $\cdots \int \delta(\mathbf{R}_{b}-t) f(\mathbf{R}_{t_{1}}\cdots ;p_{t_{t}}\cdots ;t) d\mathbf{R}_{t}\cdots d_{t_{t_{t}}}$

others are ;

 $\langle m_i \delta \left(\boldsymbol{r} - \boldsymbol{r}_i \right); f$

The total roass density at r due to all audecules is thus

 $P(z; t) - \sum_{k=1}^{N} m_k (\delta(\mathbf{R}_k - \mathbf{r}));$

 $\int P_{i}\partial(R_{k}-r)/(R_{i_{1}}\cdots ; p_{i}\cdots ; i)dR_{i_{1}}\cdots dp_{i_{r}}$

id the locations of the

 $\int \cdots \int \delta(\mathbf{R}_{1} - \mathbf{r}) f(\mathbf{R}_{1}, \cdots, \mathbf{p}_{1}, \cdots, \mathbf{j}) d\mathbf{R}_{1} \cdots d\mathbf{p}_{N}$

at the eth molecule to the momentum per unit values (mass current decas(y), "The local momentum decasity

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it is at

(2.5)

, (2.4) becomes $\frac{\partial}{\partial t} (a; f) = \sum_{i=1}^{n} \left(\sum_{m_{e_{i}}}^{p_{e_{i}}} \nabla_{R_{i}a} - \nabla_{R_{i}} \nabla_{R_{i}a} \right) (2.7) \qquad \begin{array}{c} Consecucity, (p_{i}f)(R_{i} - t), f) \text{ is the } p_{i}(a_{i}, f) = 1 \\ mean momentum by the from the product of this is the product of the interval is the second secon$

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(3.1)

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The equations of hydrodynamics (1.1), (1.2), and (1.4) are concerned with densitive in ecdancy 3-space, e.g., mass density, momentum density, and energy density. We shall now express these as the expectation values of hydramical variables over an ensemble baving distribution function f.

instruction for the probability per unit volume that the kth molecules be as $R_{\rm e}$ is $\int \cdots \int f(\mathbf{R}_{i_1} \cdots \mathbf{p}_{i_t} \cdots \mathbf{i}_t) d\mathbf{R}_1 \cdots$ $(\mathbf{R}_1, \dots, \mathbf{R}_k, \dots, \mathbf{d}_k)$ where the integration is over all position vectors are \mathcal{A}_k where \mathcal{A}_k and over all momental vectors. Introducing that the kih molecule be at t at time t is

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Selecting Functions

. The Dirac delta selects molecules at a point

- Infinitely high, infinitely thin peak
- Equivalent to the continuum differential formulation at a point

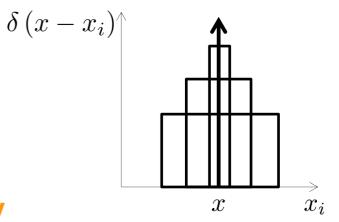
$$\rho(\mathbf{r},t) = \sum_{i=1}^{N} m_i \delta\left(\mathbf{r} - \mathbf{r}_i\right)$$

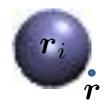


- . Other difficulties with the Dirac delta function
- . Relaxed weighting functions
 - By Hardy(1981), Hoover (2009), Murdoch (2010) and others

$$\rho(\mathbf{r},t) \approx \sum_{i=1}^{N} m_i \Delta \left(\mathbf{r} - \mathbf{r}_i\right)$$

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x

 x_i

 $\Delta (x - x_i)$

The Molecular Control Volume



Control Volume Function

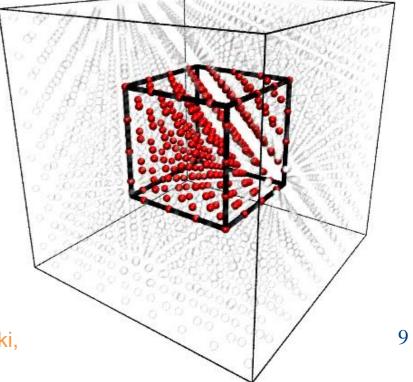
• The Control volume function is the integral of the Dirac delta function in 3 dimensions

$$\vartheta_i \equiv \int_{x^-}^{x^+} \int_{y^-}^{y^+} \int_{z^-}^{z^+} \delta(x_i - x) \delta(y_i - y) \delta(z_i - z) dx dy dz$$

$$= [H(x^{+} - x_{i}) - H(x^{-} - x_{i})]$$

$$\times [H(y^{+} - y_{i}) - H(y^{-} - y_{i})]$$

$$\times [H(z^{+} - z_{i}) - H(z^{-} - z_{i})]$$



For full details, please see E.R. Smith, D.M. Heyes, D. Dini, T.A. Zaki, Phys. Rev. E 85. 056705 (2012)

Derivatives yields the Surface Fluxes

. Taking the Derivative of the CV function

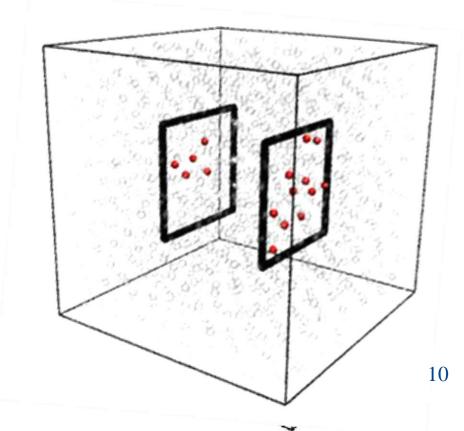
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - x_i) - \delta(x^- - x_i)\right] \\ \times \left[H(y^+ - y_i) - H(y^- - y_i)\right] \\ \times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

• Surface fluxes over the top and bottom surface

$$dS_{ix} = dS_{ix}^+ - dS_{ix}^-$$

. Vector form defines six surfaces

$$d\mathbf{S}_i = \mathbf{i} dS_{xi} + \mathbf{j} dS_{yi} + \mathbf{k} dS_{zi}$$



Applying the Control Volume Function

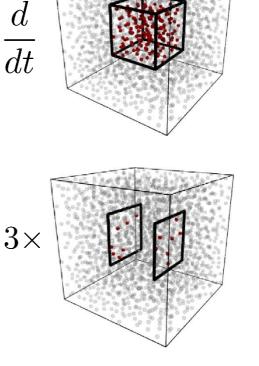
. Molecular mass in a control volume

$$\frac{d}{dt}\sum_{i=1}^{N} m_i \vartheta_i = -\sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\mathbf{S}_i \qquad \qquad \frac{\partial}{\partial t} \int_{V} \rho dV = -\oint_{S} \rho \mathbf{u} \cdot d\mathbf{S}_i$$

. Mathematical manipulation yields surface fluxes

$$\frac{d}{dt} \sum_{i=1}^{N} m_i \vartheta_i = \sum_{i=1}^{N} \left(\vartheta_i \frac{d}{dt} \mathbf{y}_i + m_i \frac{d}{dt} \vartheta_i \right)$$
$$= \sum_{i=1}^{N} m_i \frac{d\mathbf{r}_i}{dt} \cdot \frac{d}{d\mathbf{r}_i} \vartheta_i$$
$$= -\sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\mathbf{S}_i$$

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 $d\mathbf{S}$

Reynolds' Transport Theorem

. Mass, momentum and energy equations

. Mass Conservation

$$\frac{d}{dt}\sum_{i=1}^{N}m_{i}\vartheta_{i} = -\sum_{i=1}^{N}m_{i}\mathbf{v}_{i} \cdot d\boldsymbol{S}_{i}$$

Momentum Balance

$$\frac{d}{dt} \sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i = -\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i + \frac{1}{2} \sum_{i,j}^{N} \boldsymbol{f}_{ij} \vartheta_{ij}$$

$$\begin{array}{l} \mathbf{Linergy \ Conservation} \\ \frac{d}{dt} \sum_{i=1}^{N} e_{i} \vartheta_{i} = -\sum_{i=1}^{N} e_{i} \mathbf{v}_{i} \cdot d\mathbf{S}_{i} \\ + \frac{1}{2} \sum_{i=1}^{N} \sum_{i \neq j}^{N} \frac{\mathbf{p}_{i}}{m_{i}} \cdot \mathbf{f}_{ij} \vartheta_{ij} \end{array}$$

$$\frac{\partial}{\partial t} \int_{V} \rho dV = -\oint_{S} \rho \boldsymbol{u} \cdot d\mathbf{S}$$

$$\frac{\partial}{\partial t} \int_{V} \rho \boldsymbol{u} dV = -\oint_{S} \rho \boldsymbol{u} \boldsymbol{u} \cdot d\mathbf{S}$$

$$+\mathbf{F}_{ ext{surface}}$$

$$\frac{\partial}{\partial t} \int_{V} \rho \mathcal{E} dV = -\oint_{S} \rho \mathcal{E} \boldsymbol{u} \cdot d\mathbf{S}$$

$$-\oint_{S} \mathbf{\Pi} \cdot \boldsymbol{u} \cdot d\mathbf{S} + \mathbf{q} \cdot d\mathbf{S}$$

Reynolds' Transport Theorem

- Mass, momentum and energy equations
 - Mass Conservation

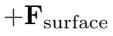
$$\frac{d}{dt}\sum_{i=1}^{N}m_i\vartheta_i = -\sum_{i=1}^{N}m_i\mathbf{v}_i \cdot d\mathbf{S}_i$$

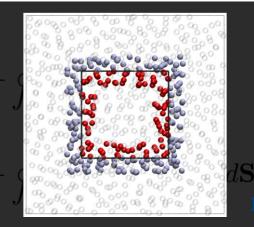
$$\frac{\partial}{\partial t} \int_{V} \rho dV = -\oint_{S} \rho \boldsymbol{u} \cdot d\mathbf{S}$$

Momentum Balance

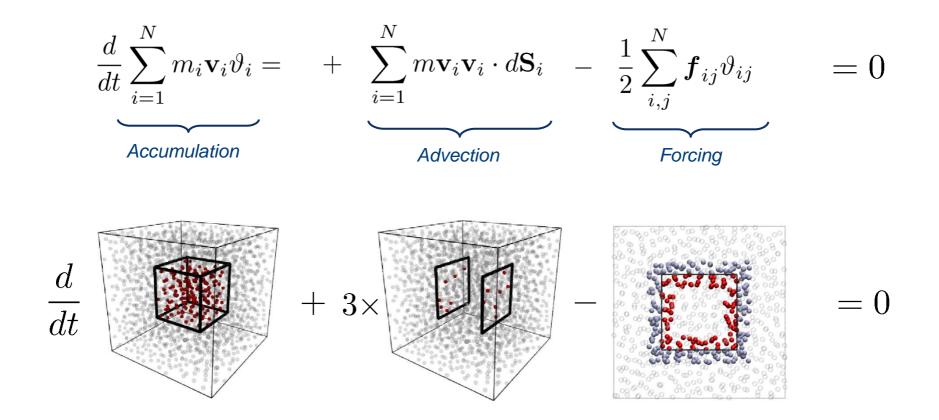
$$\frac{d}{dt} \sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i = -\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i + \frac{1}{2} \sum_{i,j}^{N} \boldsymbol{f}_{ij} \vartheta_{ij}$$

$$\frac{\partial}{\partial t} \int_{V} \rho \boldsymbol{u} dV = -\oint_{S} \rho \boldsymbol{u} \boldsymbol{u} \cdot d\mathbf{S}$$





. Momentum Balance

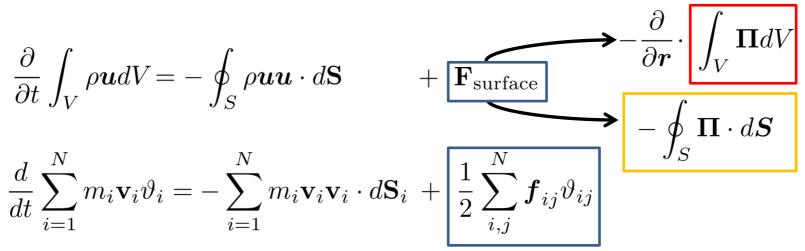


Applications



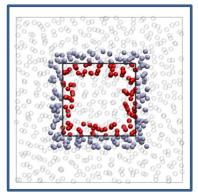
The Pressure Tensor

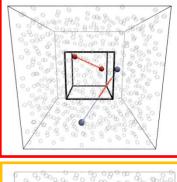
Control Volume equations in terms of the pressure tensor



. Molecular surface pressure over all 6 surfaces

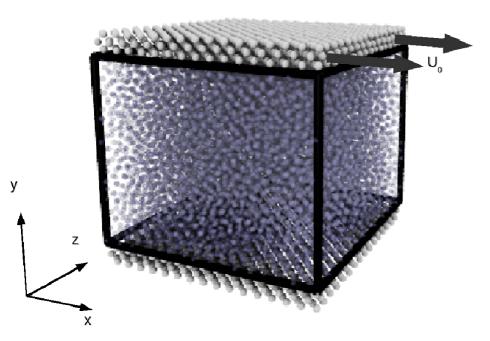
$$\begin{split} \frac{1}{2} \sum_{i,j}^{N} \boldsymbol{f}_{ij} \vartheta_{ij} &= -\frac{\partial}{\partial \boldsymbol{r}} \cdot \begin{bmatrix} \frac{1}{2} \sum_{i,j}^{N} \boldsymbol{f}_{ij} \boldsymbol{r}_{ij} \int_{0}^{1} \vartheta_{s} ds & \text{Volume Average} \\ & \text{Lutsko (1988) \&} \\ \text{Cormier et al (2001)} \end{bmatrix} \\ &= -\frac{1}{2} \sum_{i,j}^{N} \boldsymbol{f}_{ij} \boldsymbol{r}_{ij} \cdot \int_{0}^{1} \frac{\partial \vartheta_{s}}{\partial \boldsymbol{r}} ds \\ &= \begin{bmatrix} -\frac{1}{4} \sum_{i,j}^{N} \boldsymbol{f}_{ij} \left[\underline{sgn}(r_{\alpha}^{\pm} - r_{\alpha i}) - \underline{sgn}(r_{\alpha}^{\pm} - r_{\alpha j}) \right] \\ & \text{MOP (Todd et al 1995)} \end{bmatrix} S_{\alpha ij}^{\pm} \end{split}$$





. Simulation setup

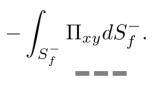
- Starting Couette flow
- . Tethered wall molecules
- Wall thermostat: Nosé-Hoover
- Averages are computed over 1000 time steps and 8 realizations

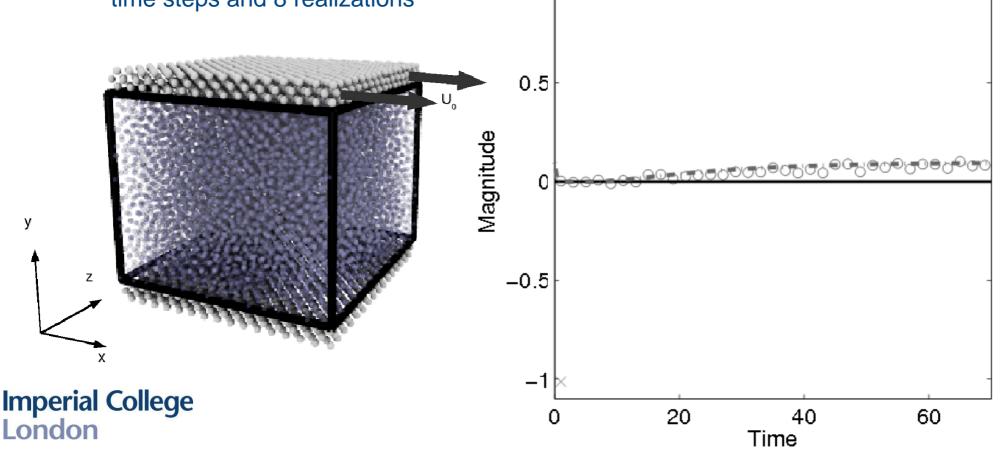


. Simulation setup

- . Starting Couette flow
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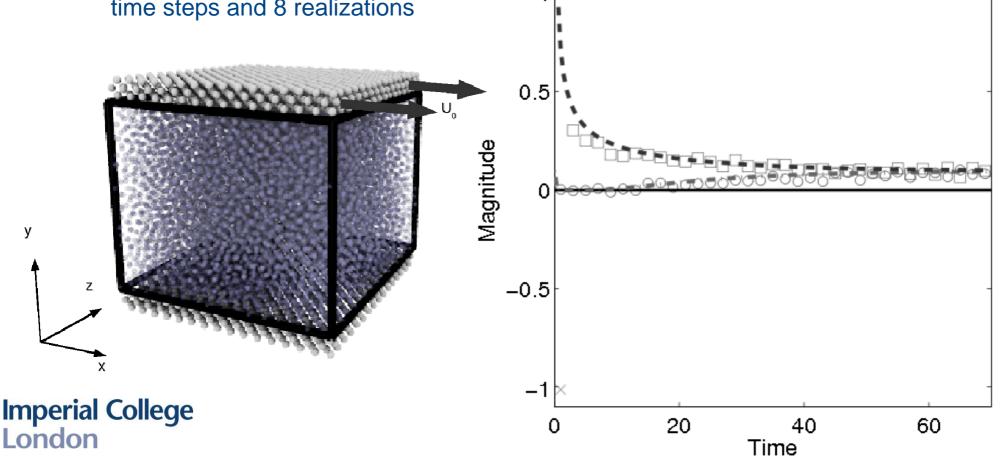




. Simulation setup

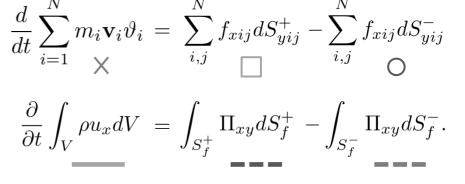
- . Starting Couette flow
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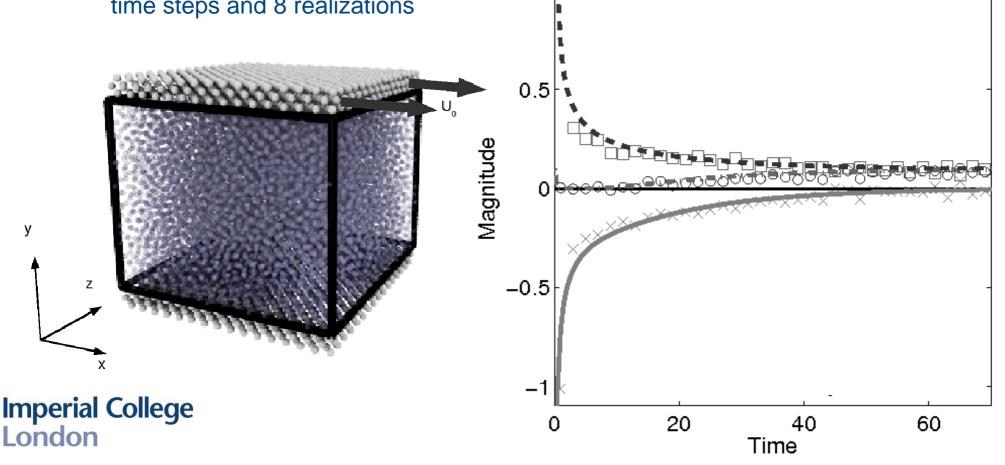
 $=\sum_{i,j}^{N} f_{xij} dS_{yij}^{+} - \sum_{i,j}^{N} f_{xij} dS_{yij}^{-}$ $= \int_{S_{f}^{+}} \Pi_{xy} dS_{f}^{+} - \int_{S_{f}^{-}} \Pi_{xy} dS_{f}^{-}.$



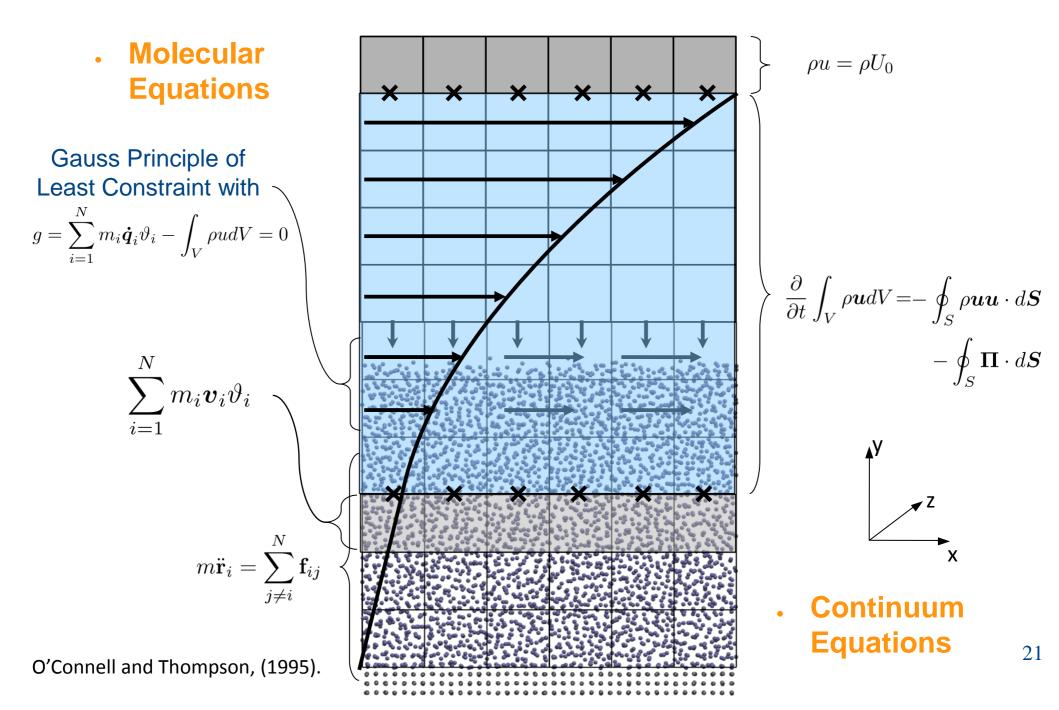
. Simulation setup

- . Starting Couette flow
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Control Volume Coupling



Summary

- Reformulated the Irving and Kirkwood (1950) equations in terms of a control volume
 - Compared to the continuum Control Volume equations not pointwise so the Dirac delta function is replaced by the CV function
 - The CV function is mathematically and computational well defined and applicable to any discrete system
- Derivation of discrete CV equations
 - Not an approximation of the Dirac delta but an integration over a volume
 - Exactly conservative equations derived for mass, momentum and energy
- Applications
 - Provides insight into the pressure tensors and link them to time evolution
 - Arbitrary CV shapes and exact conservation can be exploited
 - Can be used in the derivation of localised constraint algorithms using minimisation principles (e.g. Gauss' Least Constraint)

References

. References

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E.R. Smith, D.M. Heyes, D. Dini, T.A. Zaki, Phys. Rev. E 85. 056705 (2012)

Acknowledgements:

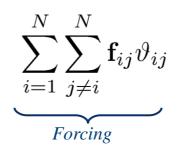
- Professor David Heyes
- Dr Daniele Dini
- Dr Tamer Zaki

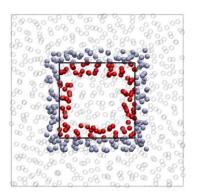
Thank you for listening Any Questions?

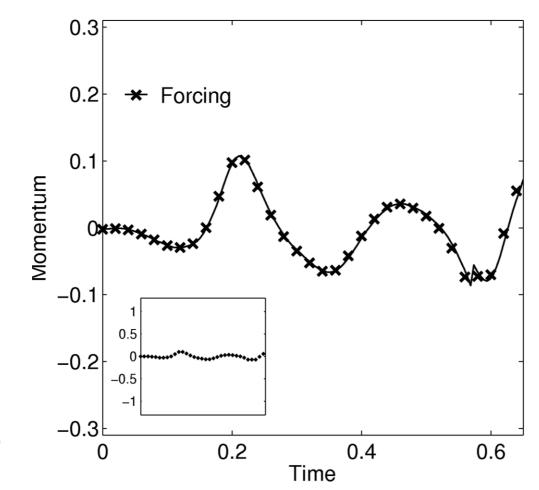
Extra Material



. Momentum Balance

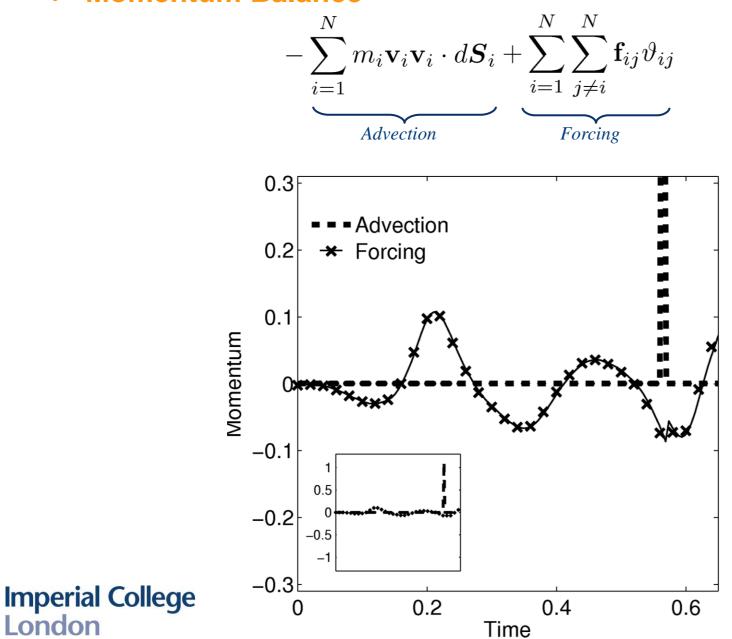


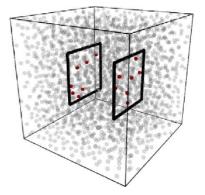


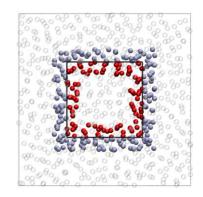


Momentum Balance

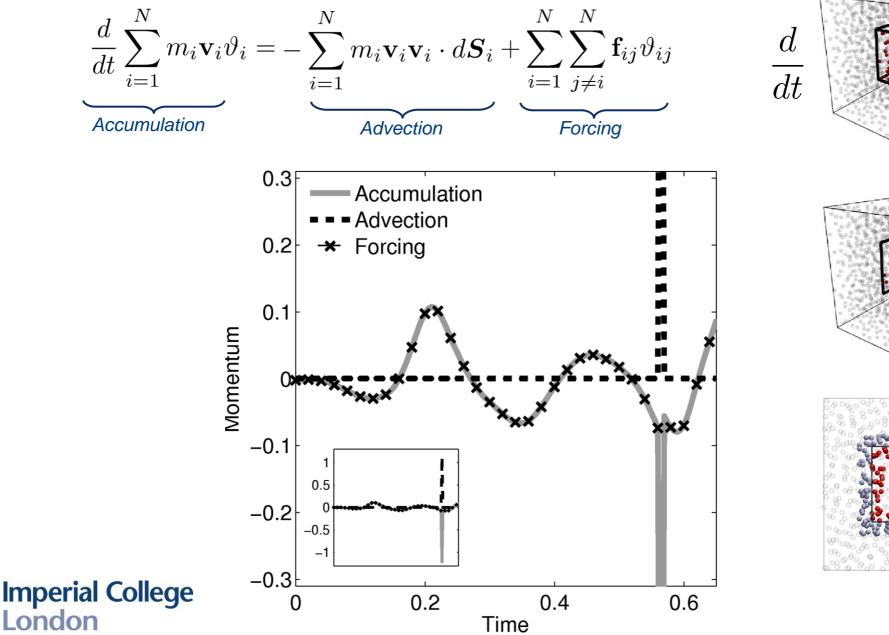
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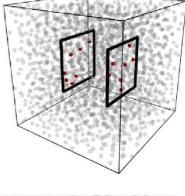


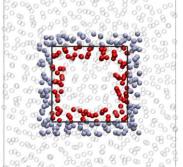




. Momentum Balance







Control Volume Function (revisited)

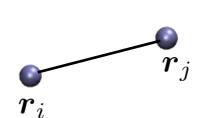
• The Control volume function is the integral of the Dirac delta function in 3 dimensions

$$\vartheta_i \equiv \int_V \delta(\mathbf{r} - \mathbf{r}_i) \, dV$$

= $\begin{bmatrix} H(x^+ - x_i) - H(x^- - x_i) \end{bmatrix}$
× $\begin{bmatrix} H(y^+ - y_i) - H(y^- - y_i) \end{bmatrix}$
× $\begin{bmatrix} H(z^+ - z_i) - H(z^- - z_i) \end{bmatrix}$

• Replace molecular position with equation for a line

$$m{r}_i
ightarrow m{r}_i - s m{r}_{ij}$$



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For full details, please see E.R. Smith, D.M. Heyes, D. Dini, T.A. Zaki, Phys. Rev. E 85. 056705 (2012)

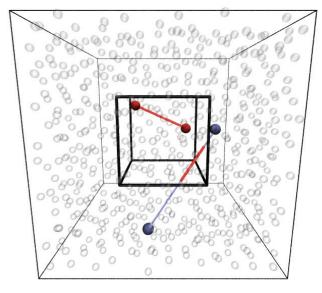
Control Volume Function (revisited)

• The Control volume function is the integral of the Dirac delta function in 3 dimensions

$$\vartheta_s \equiv \int_V \delta(\mathbf{r} - \mathbf{r}_i + s\mathbf{r}_{ij})dV = \begin{bmatrix} H(x^+ - x_i + sx_{ij}) - H(x^- - x_i + sx_{ij}) \end{bmatrix} \\ \times \begin{bmatrix} H(y^+ - y_i + sy_{ij}) - H(y^- - y_i + sy_{ij}) \end{bmatrix} \\ \times \begin{bmatrix} H(z^+ - z_i + sz_{ij}) - H(z^- - z_i + sz_{ij}) \end{bmatrix}$$

. Length of interaction inside the CV

$$\ell_{ij} = \int_{0}^{1} \vartheta_s ds$$



Derivatives Yield the Surface Forces

. Taking the Derivative of the CV function

$$\frac{\partial \vartheta_s}{\partial x} \equiv \left[\delta(x^+ - x_i + sx_{ij}) - \delta(x^- - x_i + sx_{ij}) \right] \\ \times \left[H(y^+ - y_i + sy_{ij}) - H(y^- - y_i + sy_{ij}) \right] \\ \times \left[H(z^+ - z_i + sz_{ij}) - H(z^- - z_i + sz_{ij}) \right]$$

30

• Surface fluxes over the top and bottom surface

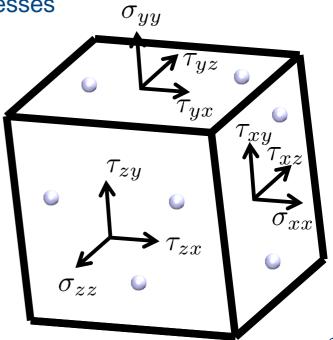
$$dS_{xij} \equiv \int_{0}^{1} \frac{\partial \vartheta_s}{\partial x} ds = dS_{xij}^{+} - dS_{xij}^{-}$$

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London
$$dS_{xij}^{+} = \frac{1}{2} \underbrace{\left[sgn(x^{+} - x_{i}) - sgn(x^{+} - x_{j})\right]}_{MOP} S_{xij}$$

More on the Pressure Tensor

. Extensive literature on the form of the molecular stress tensor

- No unique solution Schofield, Henderson (1988)
- Two key forms in common use Volume Average (Lutsko, 1988) and Method of Planes (Todd et al 1995)
- . Link provided between these descriptions
 - Through formal manipulation of the functions
 - Exposes the relationship between the molecular stresses and the evolution of momentum
- In the limit the Dirac delta form of Irving and Kirkwood (1950) is obtained
 - This suggests the same limit is not possible in the molecular system
 - Arbitrary stress based on the volume of interest



Moving reference frame

- Why the continuum form of Reynolds' transport theorem has a partial derivative but the discrete is a full derivative
 - Eulerian mass conservation

$$\frac{d}{dt}\sum_{i=1}^{N}m_i\vartheta_i = -\sum_{i=1}^{N}m_i\mathbf{v}_i \cdot d\boldsymbol{S}_i$$

$$\vartheta_i = \vartheta_i(\boldsymbol{r}_i(t), \boldsymbol{r})$$

$$\frac{\partial}{\partial t} \int_{V} \rho dV = -\oint_{S} \rho \boldsymbol{u} \cdot d\mathbf{S}$$

Lagrangian mass conservation

$$\frac{d}{dt}\sum_{i=1}^{N} m_i \vartheta_i = -\sum_{i=1}^{N} m_i \left(\mathbf{v}_i + \overline{\boldsymbol{u}}\right) \cdot d\boldsymbol{S}_i$$

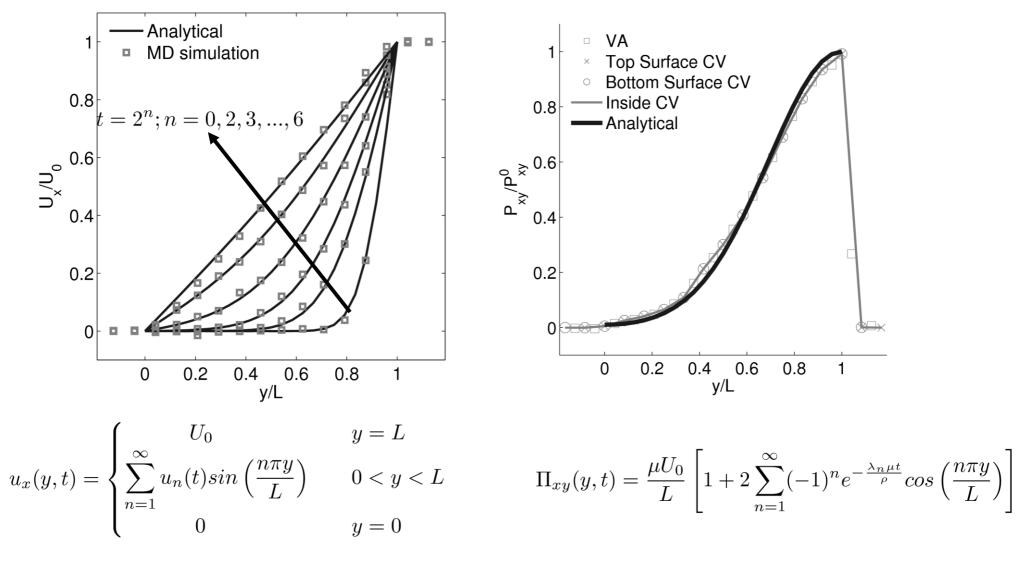
 $\overline{\boldsymbol{u}} \cdot d\boldsymbol{S}_i = \frac{d\boldsymbol{r}}{dt} \cdot \frac{d\vartheta_i}{d\boldsymbol{r}}$

$$\vartheta_i = \vartheta_i(\boldsymbol{r}_i(t), \boldsymbol{r}(t))$$

$$\frac{d}{dt} \int_{V} \rho dV = \oint_{S} \rho \left(\boldsymbol{u} - \overline{\boldsymbol{u}} \right) \cdot d\boldsymbol{S}$$

$$\oint_{S} \rho \boldsymbol{u} \cdot d\boldsymbol{S} - \oint_{S} \rho \overline{\boldsymbol{u}} \cdot d\boldsymbol{S} = 0$$

Continuum Analytical Couette Flow



Where, $\lambda_n = \left(\frac{n\pi}{L}\right)^2$ and $u_n(t) = \frac{2U_0(-1)^n}{n\pi} \left(e^{-\frac{\lambda_n \mu t}{\rho}} - 1\right)$ **Imperial College** London
33

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Continuum Analytical

• Simplify the momentum balance (Navier-Stokes) equation

$$\frac{\partial}{\partial t}\boldsymbol{u} + \boldsymbol{\nabla} \cdot \boldsymbol{u} \boldsymbol{u} = \frac{1}{\rho} \boldsymbol{\nabla} \boldsymbol{P} + \frac{\mu}{\rho} \boldsymbol{\nabla}^2 \boldsymbol{u}$$

• Solve the 1D unsteady diffusion equation.

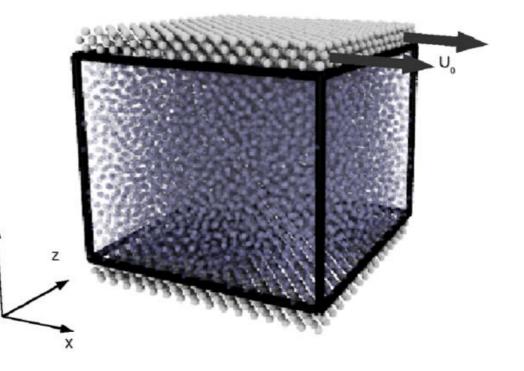
$$\frac{\partial u_x}{\partial t} = \frac{\mu}{\rho} \frac{\partial^2 u_x}{\partial y^2}$$

• With Boundary Conditions

$$u_x(0,t) = 0$$
$$u_x(L,t) = U_0$$
$$u_x(y,0) = 0$$

• Molecular Dynamics

• Fixed bottom wall, sliding top wall with both thermostatted



Continuum Analytical

• Simplify the control volume momentum balance equation

$$\frac{\partial}{\partial t} \int_{V} \rho \boldsymbol{u} dV = -\oint_{S} \rho \boldsymbol{u} \boldsymbol{u} \cdot d\boldsymbol{S}$$
$$-\oint_{S} P \boldsymbol{I} \cdot d\boldsymbol{S} + \oint_{S} \boldsymbol{\sigma} \cdot d\boldsymbol{S}$$

. Simplifies for a single control volume

$$\frac{\partial}{\partial t}\int_{V}\!\!\!\!\rho u_{x}dV\!=\!\int_{S_{y}^{+}}\!\!\!\!\!\sigma_{xy}dS_{f}^{+}\!-\!\int_{S_{f}^{-}}\!\!\!\!\!\sigma_{xy}dS_{y}^{-}$$

• With Boundary Conditions

$$u_x(0,t) = 0$$
$$u_x(L,t) = U_0$$
$$u_x(y,0) = 0$$

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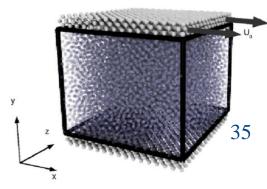
- Molecular Dynamics
 - Discrete form of the Momentum balance equation

$$\frac{d}{dt} \sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i = -\oint_S \rho \boldsymbol{u} \boldsymbol{u} \cdot d\boldsymbol{S}$$
$$-\sum_{i=1}^{N} (\boldsymbol{v}_i - \boldsymbol{u}) (\boldsymbol{v}_i - \boldsymbol{u}) \cdot d\boldsymbol{S}_i - \sum_{i=1}^{N} \sum_{j \neq i}^{N} \varsigma_{ij} \cdot d\boldsymbol{S}_{ij}$$

• Simplifies for a single control volume

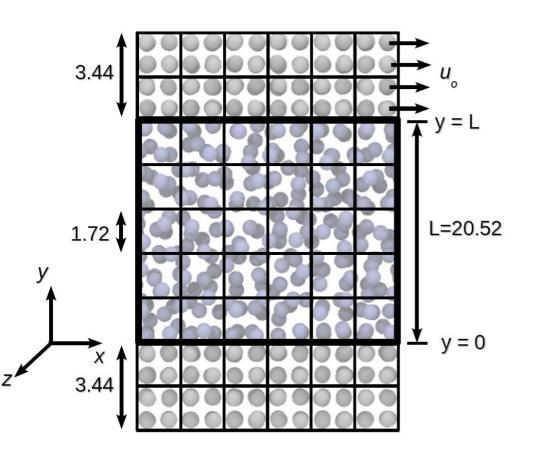
$$\frac{d}{dt}\sum_{i=1}^{N}m_i\mathbf{v}_i\vartheta_i = \sum_{i,j}^{N}f_{xij}dS_{yij}^+ - \sum_{i,j}^{N}f_{xij}dS_{yij}^-$$

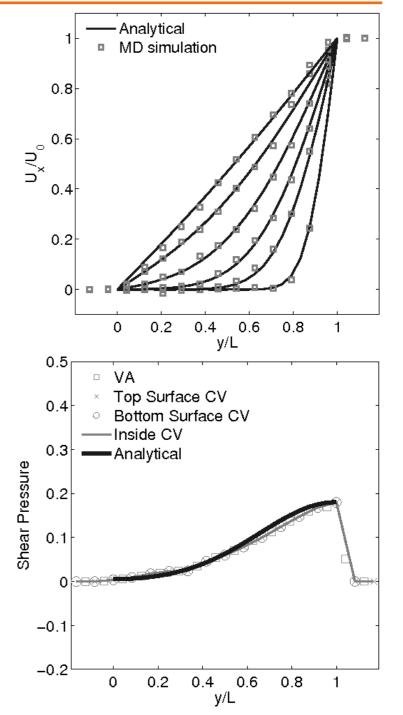
• Fixed bottom wall, sliding top wall with both thermostatted



. Simulation setup

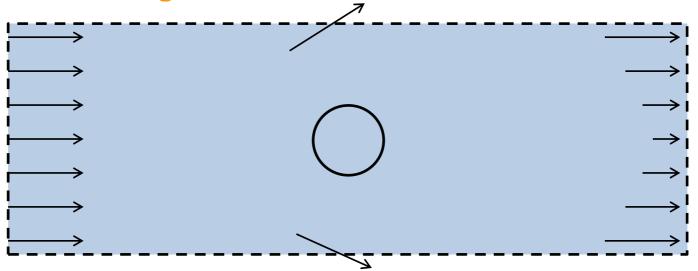
- Starting Couette flow
- · Wall thermostat: Nosé-Hoover
- Averages are computed over 1000 time steps and 8 realizations



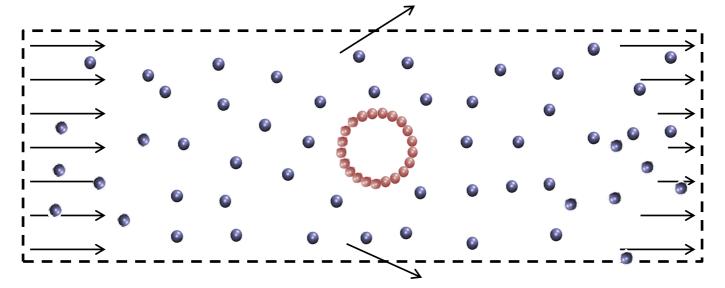


Flow past a cylinder

. Use of the momentum conservation of the control volume to determine the drag coefficient



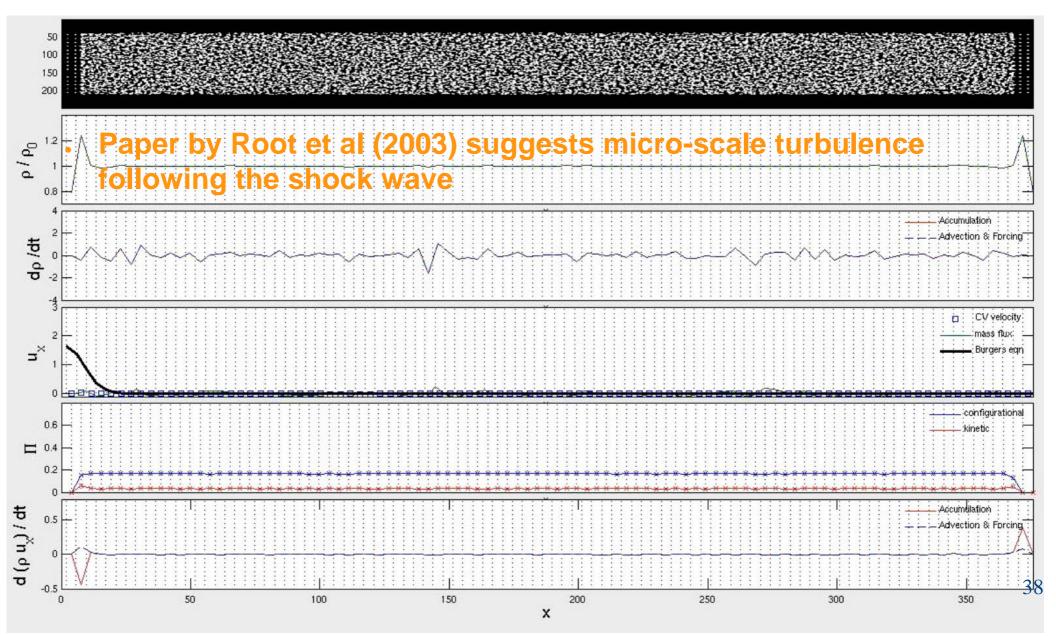
. Drag over a Carbon Nano-tube can be determined



Shockwaves

Current work on application of control volume theory

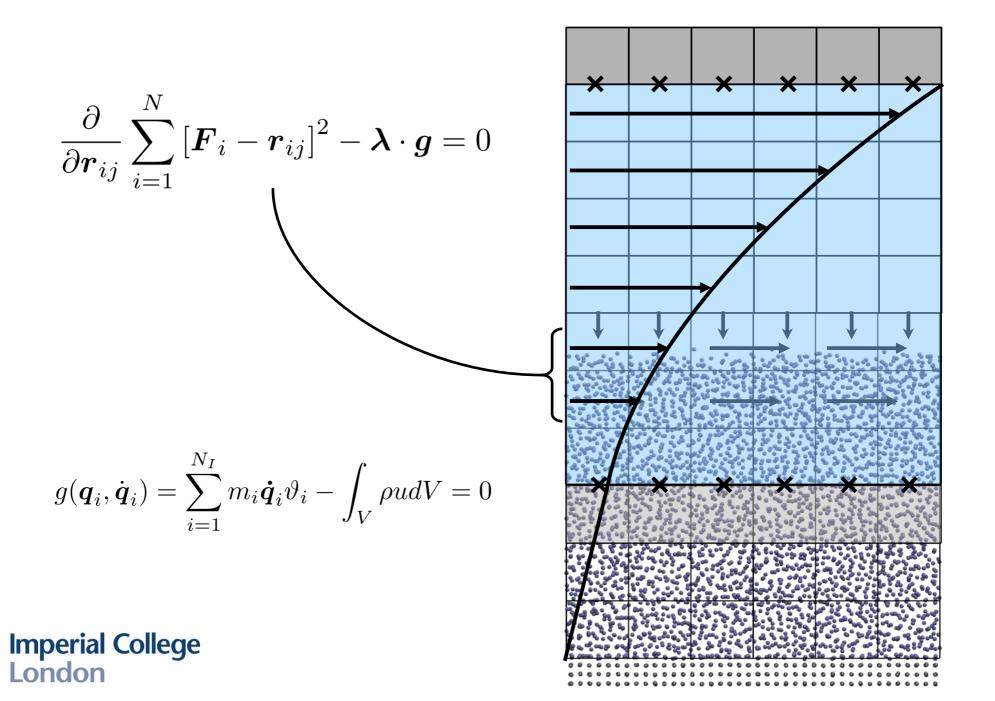
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Constrained dynamics for coupling



Control Volume Coupling



Constrained Control Volume

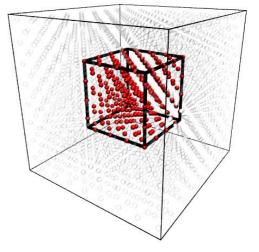
- . We want to apply a constraint of the form
 - . Control Volume momentum in both domains fixed to the same value

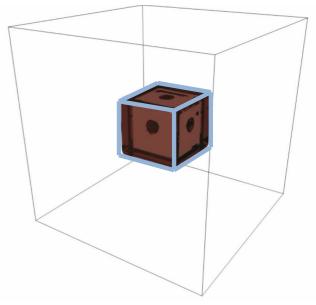
$$g(\boldsymbol{q}_i, \dot{\boldsymbol{q}}_i) = \sum_{i=1}^{N} m_i \dot{\boldsymbol{q}}_i \vartheta_i - \int_{V} \rho u dV = 0$$

. The molecular Control Volume is given by

$$\vartheta_i \equiv \int_V \delta(\mathbf{r} - \mathbf{r}_i) \, dV$$

= $\left[H(x^+ - x_i) - H(x^- - x_i) \right]$
× $\left[H(y^+ - y_i) - H(y^- - y_i) \right]$
× $\left[H(z^+ - z_i) - H(z^- - z_i) \right]$





Constrained Control Volume

- . We want to apply a constraint of the form
 - . Control Volume momentum in both domains fixed to the same value

$$g(\boldsymbol{q}_i, \dot{\boldsymbol{q}}_i) = \sum_{i=1}^{N} m_i \dot{\boldsymbol{q}}_i \vartheta_i - \int_{V} \rho u dV = 0$$

- . Several methods for doing this
 - Principle of Least Action (subject to constraint)

$$\delta A_c = \delta \int_a^b \left(\mathcal{L} + \boldsymbol{\lambda} \cdot \boldsymbol{g} \right) dt = 0$$

ist Action $rac{\partial}{\partial r_{ii}}\sum_{i=1}^{N}[F_{ii}]$

$$\frac{\partial}{\partial \boldsymbol{r}_{ij}} \sum_{i=1}^{n} \left[\boldsymbol{F}_i - \boldsymbol{r}_{ij} \right]^2 - \boldsymbol{\lambda} \cdot \boldsymbol{g} = 0$$

$$\mathcal{H}_c = \mathcal{H} + oldsymbol{\lambda} \cdot oldsymbol{g}$$

. Gauss' Principle of Least Action

Extra terms in the Hamiltonian?
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Principle of least action

- . If the constraint is semi-holonomic, i.e.
 - The constraint 'g' can be integrated
 - . Alternatively/equivalently the constraint satisfies the condition (Flannery 2004)

$$\frac{d}{dt}\frac{\partial g}{\partial \dot{q}_i} - \frac{\partial g}{\partial q_i} = 0$$

- The result is the Euler-Lagrange equation is applicable in the form
 - Lagrangian in constrained form
 - Resulting equation is equivalent to the one obtained from Gauss' principle

$$\frac{d}{dt}\frac{\partial \mathcal{L}_c}{\partial \dot{q}_i} - \frac{\partial \mathcal{L}_c}{\partial q_i} = 0 \qquad \qquad \mathcal{L}_c = \mathcal{L} + \lambda g$$

Resulting equations

. Can be written in terms of the peculiar momentum

$$p_i = \frac{\partial \mathcal{L}_c}{\partial \dot{q}_i} \qquad \qquad \dot{p}_i = \frac{\partial \mathcal{L}_c}{\partial q_i}$$

. To give equations in the form

$$\dot{\boldsymbol{q}}_{i} = \frac{\boldsymbol{p}_{i}}{m_{i}} - \frac{\vartheta_{i}}{M_{I}} \left[\sum_{n=1}^{N} \boldsymbol{p}_{n} \vartheta_{n} - \int_{V} \rho \boldsymbol{u} dV \right]$$
$$\dot{\boldsymbol{p}}_{i} = \boldsymbol{F}_{i} - \frac{m_{i} \dot{\boldsymbol{q}}_{i} \cdot d\boldsymbol{S}_{i}}{M_{I}} \left[\sum_{n=1}^{N} \boldsymbol{p}_{n} \vartheta_{n} - \int_{V} \rho \boldsymbol{u} dV \right]$$



Combining the equations

. Differentiating q dot and inserting into the other

$$\ddot{\boldsymbol{q}}_{i} = \frac{\dot{\boldsymbol{p}}_{i}}{m_{i}} - \frac{d}{dt} \left(\frac{\vartheta_{i}}{M_{I}} \left[\sum_{n=1}^{N} \boldsymbol{p}_{n} \vartheta_{n} - \int_{V} \rho \boldsymbol{u} dV \right] \right)$$

$$\dot{\boldsymbol{p}}_{i} = \boldsymbol{F}_{i} - \frac{m_{i} \dot{\boldsymbol{q}}_{i} \cdot d\boldsymbol{S}_{i}}{M_{I}} \left[\sum_{n=1}^{N} \boldsymbol{p}_{n} \vartheta_{n} - \int_{V} \rho \boldsymbol{u} dV \right]$$

• Give the following equation – equivalent to one obtained by Gauss principle of Least constraint

$$m_i \ddot{\boldsymbol{q}}_i = \boldsymbol{F}_i + \frac{m_i \vartheta_i}{M_I} \left[\frac{d}{dt} \int_V \rho \boldsymbol{u} dV - \sum_{n,m}^{N} \boldsymbol{f}_{nm} \vartheta_{nm} + \sum_{n=1}^{N} m_i \dot{\boldsymbol{q}}_n \dot{\boldsymbol{q}}_n \cdot d\mathbf{S}_n \right]$$

Questions

- Is energy conserved by this semi-holonomic constraint? How can we prove this?
- This is a differential constraint it doesn't seem to work in practice. Is this a mistake?
- . Should we instead try to constrain the mass?
- . Localisation of SLLOD possible?
- . Nose Hoover style constraint possible is this preferable?

