Graeme A. Bird Plenary Lecture

DSMC: A Statistical Mechanics Perspective

Alejandro L. Garcia

San Jose State University &

Lawrence Berkeley National Lab

SJSU SAN JOSÉ STATE UNIVERSITY

BERKELEY LAB

Five Short Stories

This talk describes Direct Simulation Monte Carlo as viewed from the perspective of statistical mechanics.

- DSMC & Molecular Dynamics – Brothers separated at birth
- DSMC equation of state – Why ideal gas law?
- Transport in DSMC – A lesson from Molecular Dynamics
- Statistical fluctuations – One man's garbage…
- Second Law of Thermodynamics – Exorcising the demons

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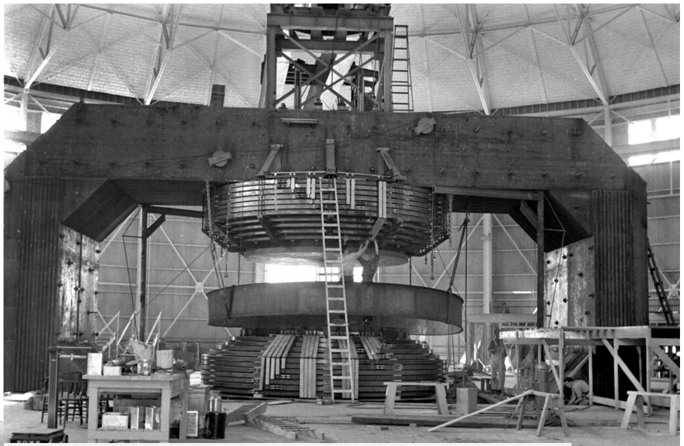
The Atomic Age

In the mid-20th century, the world entered the Atomic Age.


184 inch Cyclotron, Berkeley Lab (1942)


J. Robert Oppenheimer

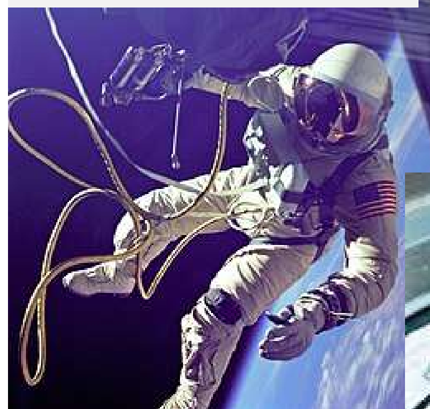

Calder Hall, UK the world's first commercial nuclear power station (1956)


First nuclear reactor: Chicago Pile-1 (1942)

The Space Age

Almost simultaneously we also entered the Space Age…

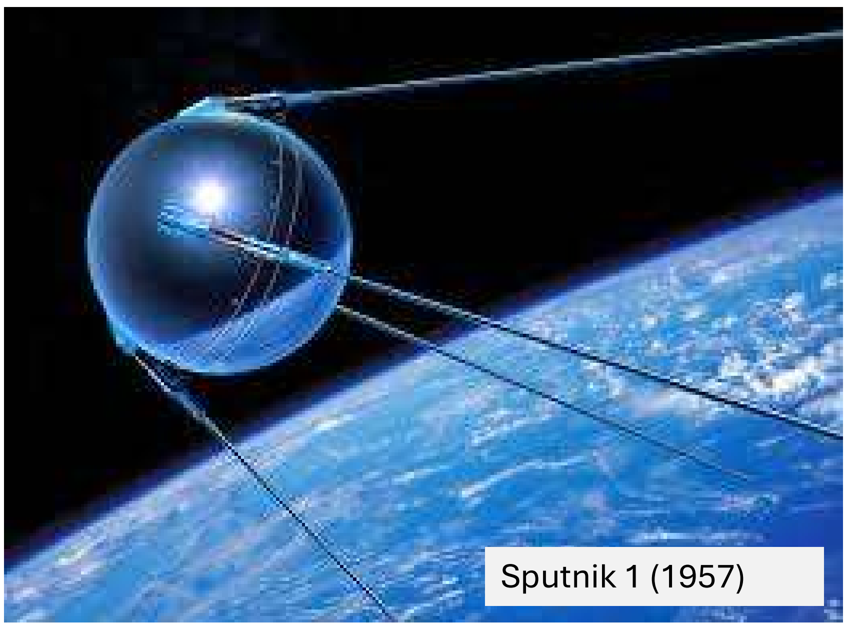
Gemini IV space walk (1965)



Cosmonaut Yuri Gagarin

Mercury-Redstone 2 space rocket (1961)

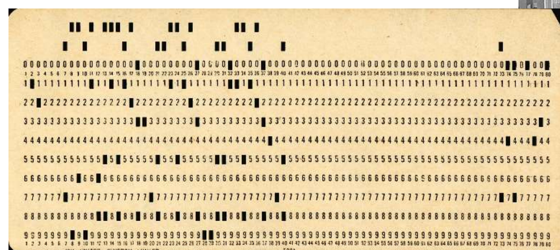
May Day, Moscow (1960)

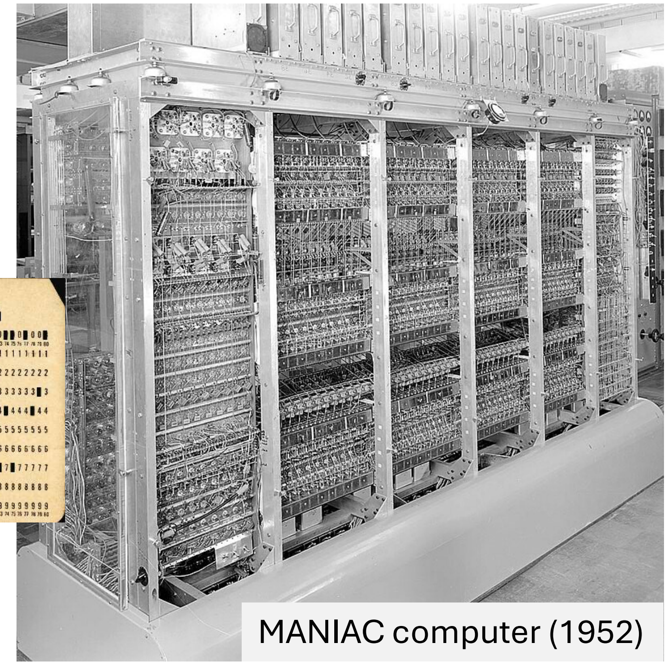


Sputnik 1 (1957)

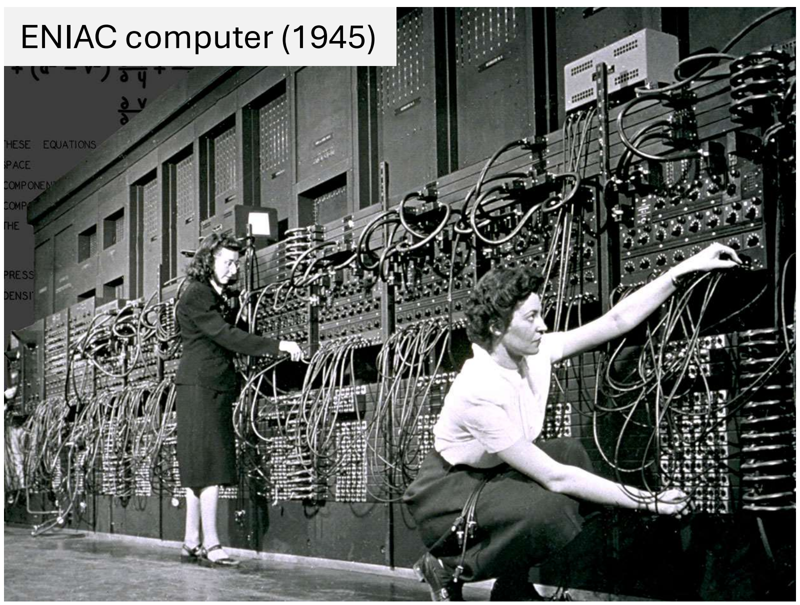
The Computer Age

… and the Computer Age.
These three eras were scientifically intertwined.





MANIAC computer (1952)



ENIAC computer (1945)

Rear Admiral Grace Hopper,
creator of COBOL

Metropolis Monte Carlo

Atomic / Nuclear Applications

1953

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 21, NUMBER 6 JUNE, 1953

Equation of State Calculations by Fast Computing Machines

NICHOLAS METROPOLIS, ARIANNA W. ROSENBLUTH, MARSHALL N. ROSENBLUTH, AND AUGUSTA H. TELLER,
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

AND

EDWARD TELLER,* *Department of Physics, University of Chicago, Chicago, Illinois*

(Received March 6, 1953)

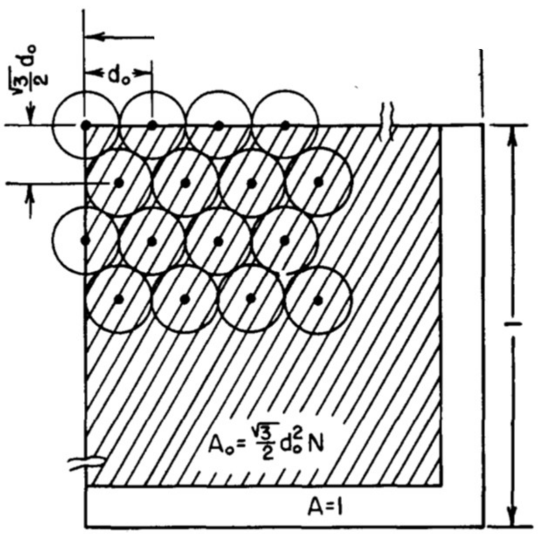


FIG. 3. The close-packed arrangement for determining A_0.

Particle algorithm to explore equilibrium phase space to estimate thermodynamic properties, such as equation of state.

No dynamics in Metropolis Monte Carlo so it could **<u>not</u>** calculate transport properties, such as viscosity.

President Kennedy with Edward and Augusta Teller

Molecular Dynamics (MD)

Atomic / Nuclear Applications

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 31, NUMBER 2 AUGUST, 1959

1959

Studies in Molecular Dynamics. I. General Method*

B. J. ALDER AND T. E. WAINWRIGHT

Lawrence Radiation Laboratory, University of California, Livermore, California

(Received February 19, 1959)

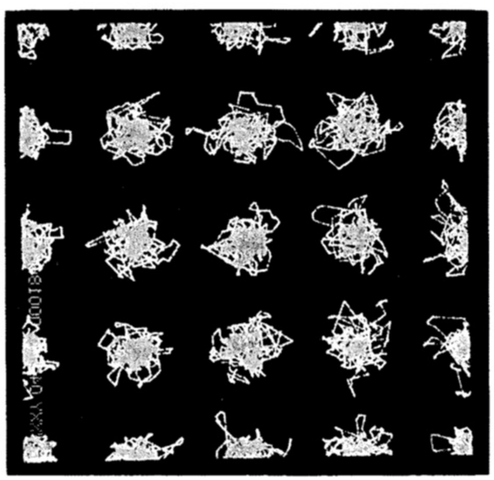


FIG. 2. The traces of 32 hard sphere particles in the periodic boundary conditions in the solid phase for about 3000 collisions.

Molecular Dynamics included the effect of intermolecular forces (at first only hard spheres) on the trajectories of particles.

MD could calculate thermodynamic ***and*** transport properties for fluids at extreme pressures and temperatures.

Berni Alder, Thomas Wainwright, Mary Ann Mansigh (clockwise, from top)

Direct Simulation Monte Carlo

Space / Missile Applications

1963

Approach to Translational Equilibrium in a Rigid Sphere Gas

G. A. Bird
Department of Aeronautical Engineering, University of Sydney, Sydney, Australia
(Received 10 May 1963)

Using the Silliac digital computer in the University of Sydney, more than 30 000 collisions were computed per hour of computing time. The results quoted below are based on the mean of ten runs each involving 500 molecules. As a check on the accuracy of the Monte Carlo-type approach, the mean free path and the collision frequency were calculated by assigning the appropriate time interval to each

G.A. Bird, *Phys. Fluids* **6**, 1518–1519

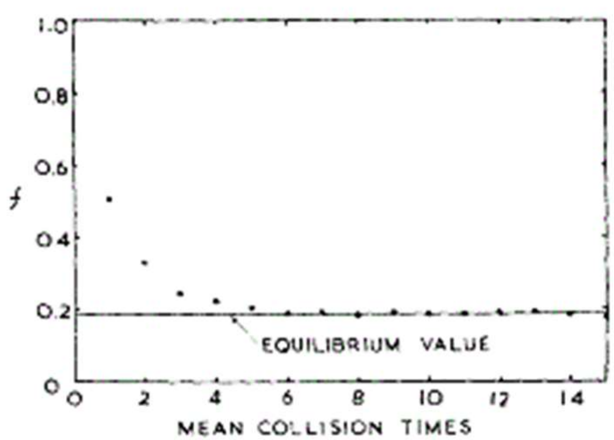


FIG. 2. Fraction of molecules in range 0.9 to 1.1 v_a.

DSMC was similar to MD but used a random collision algorithm instead of calculating deterministic trajectories.

Not related to Metropolis MC except that events occur by an Accept / Reject process (moves in MMC, collisions in DSMC).

Graeme Bird

DSMC & MD - Brothers Separated at Birth

Berni Alder

1959 MD

Statistical Mechanics

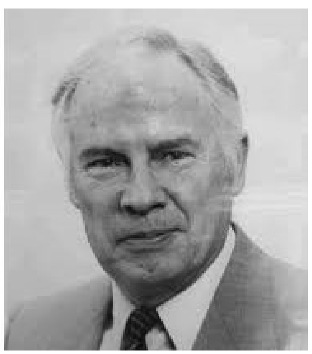
20th century

Equations of State
Transport coefficients

21st century

Molecular Chemistry
Cellular Biology

Common Ground



Graeme Bird

1963 DSMC

Kinetic Theory

20th century

Hypersonic Flow
Transition Regime

21st century

Nanofluidics
Plasma, granular, planetary, etc.

Alder and Bird finally met at the 2000 RGD in Sydney

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Berni Alder & DSMC

In 1989 I joined the faculty at San Jose State University, located in Silicon Valley.
Met Berni Alder and started working with him at the nearby Livermore Lab.

Alder took an interest in DSMC and we eventually published 16 papers, most of them on ways to extend the DSMC algorithm.

When I first explained DSMC to Berni he asked, “But why does it give the ideal gas law?”

Berni Alder

Berni Alder awarded the Boltzmann medal in 2001

MD Equation of State

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 33, NUMBER 5 NOVEMBER, 1960

Studies in Molecular Dynamics. II. Behavior of a Small Number of Elastic Spheres

B. J. ALDER AND T. E. WAINWRIGHT
Lawrence Radiation Laboratory, University of California, Livermore, California

Molecular dynamics simulations of Alder, Wainwright, and Mansigh had measured the equation of state for hard spheres and found good agreement with Enskog theory and Metropolis Monte Carlo results.

The particle diameter, *d*, is used in DSMC collisions yet it does *not* affect the equation of state.

N = 32 particles

System Volume	$\frac{pV}{NkT} - 1$
1.65000	8.41
1.70000	7.83
1.75000	7.13
1.80000	6.59
2.00000	4.89
3.00000	2.09
9.00000	0.409
10.00000	0.343
14.14214	0.249

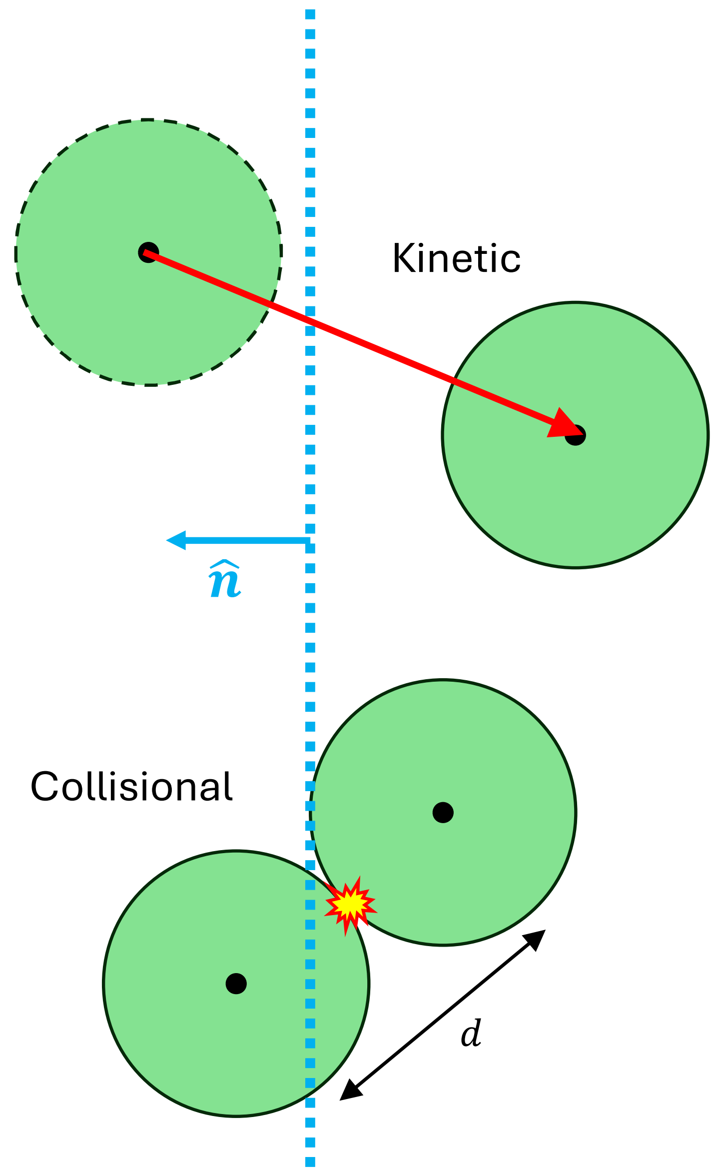
Pressure

Pressure can be defined from the rate at which momentum transfer occurs normal to a plane.

Kinetic transfer occurs as particles carry their momentum across the plane.

Collisional transfer occurs as particles on opposite sides exchange momentum.

An ideal gas has only kinetic transfer.



Molecular Dynamics Collisions

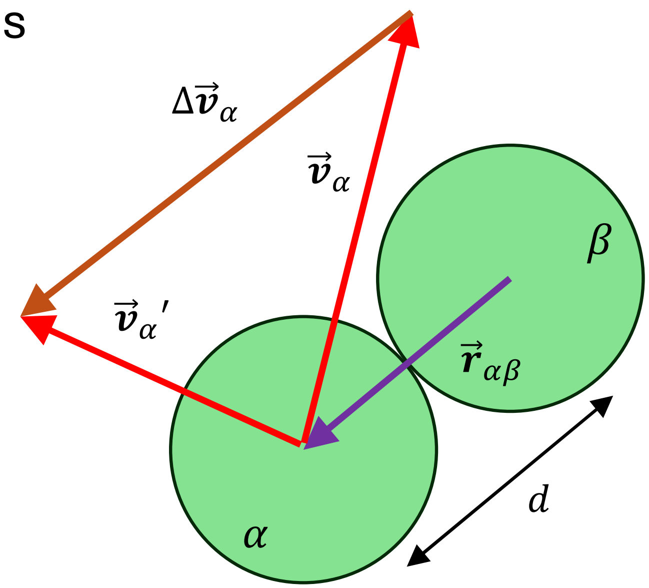
For hard sphere collisions the equation of state is

$$p = nkT + \tfrac{1}{3}\, m\, \Gamma\, \Theta$$

where Γ is the collision rate and

$$\Theta = \langle \Delta\vec{\boldsymbol{v}}_\alpha \cdot \vec{\boldsymbol{r}}_{\alpha\beta} \rangle > 0$$

is the *virial*, which depends on the particle diameter since $|\vec{\boldsymbol{r}}_{\alpha\beta}| = d$.



Obtain the equation of state in MD by measuring the collision rate and the virial.

DSMC Collisions

In DSMC, collisions occur at a distance *however*, the probability of a collision is *independent* of the particle positions within a collision cell so

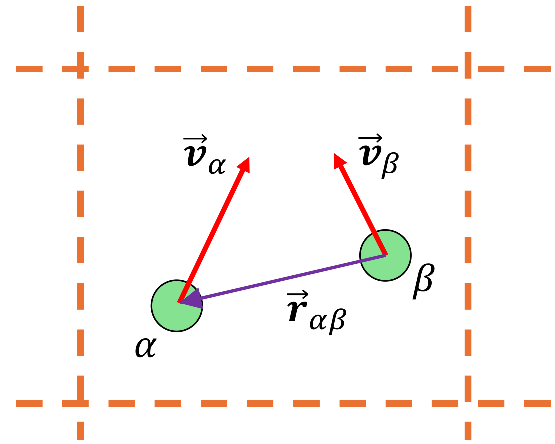
$$\langle \vec{\boldsymbol{r}}_{\alpha\beta} \rangle = 0 \qquad \text{and} \qquad \langle \Delta\vec{\boldsymbol{v}}_{\alpha} \cdot \vec{\boldsymbol{r}}_{\alpha\beta} \rangle = \langle \Delta\vec{\boldsymbol{v}}_{\alpha} \rangle \cdot \langle \vec{\boldsymbol{r}}_{\alpha\beta} \rangle$$

so

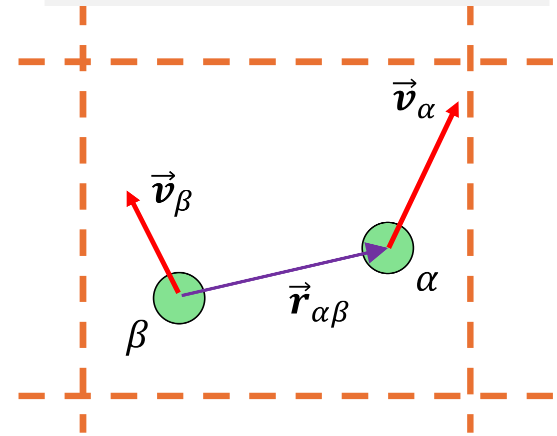
$$\Theta = \langle \Delta\vec{\boldsymbol{v}}_{\alpha} \cdot \vec{\boldsymbol{r}}_{\alpha\beta} \rangle = 0$$

The virial contribution to the pressure is zero and the equation of state for DSMC is the ideal gas law.

When I told Berni that this was because DSMC solved the Boltzmann equation he said, “The Boltzmann equation is inconsistent!”

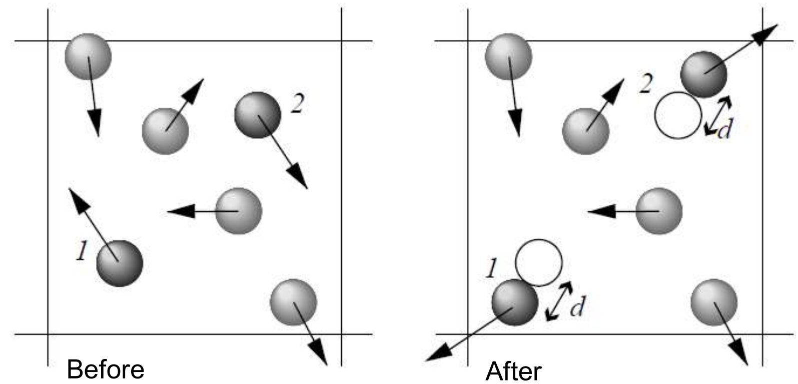


Equivalent DSMC collisions within a collision cell



CBA Collisions

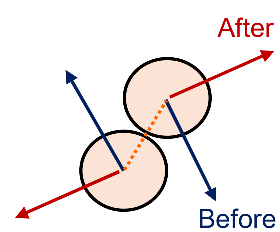
The Consistent Boltzmann Algorithm (CBA) is identical to DSMC except that collisions change both the velocities *and* the positions of colliding particles.



After computing the post-collision velocities, shift the positions as

$$\vec{r}'_\alpha = \vec{r}_\alpha + d\,\Delta\hat{v}_\alpha \qquad \vec{r}'_\beta = \vec{r}_\beta - d\,\Delta\hat{v}_\alpha$$

Direction is along the apse line (line between their centers) for a hard sphere collision with the same change in the velocity.



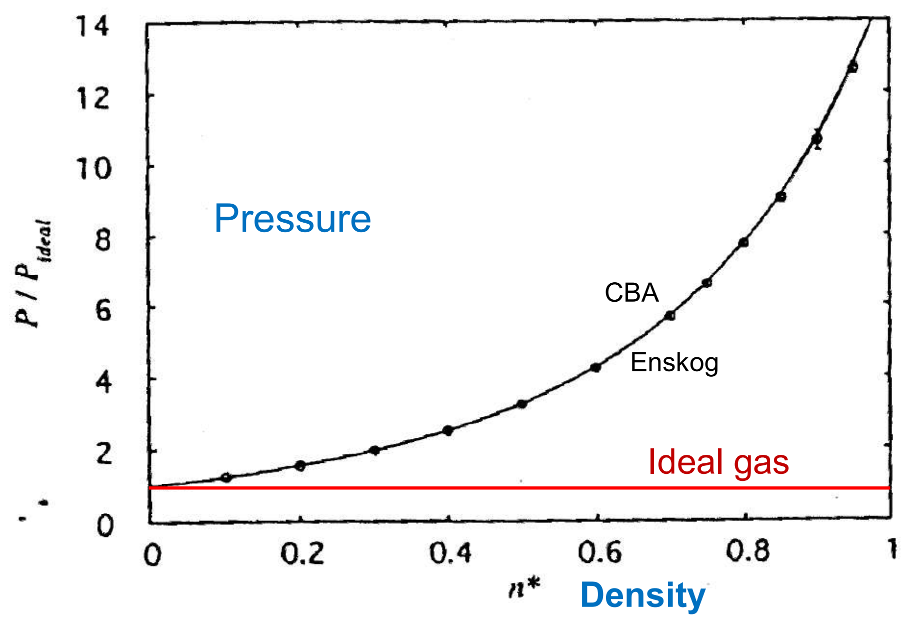
F. Alexander, A. Garcia, and B. Alder, *Phys. Rev. Lett.* **74** 5212 (1995)
A. Garcia, W. Wagner, *J. Stat. Phys.* **101** 1065 (2000)

Non-ideal Pressure in CBA

F. Alexander, A. Garcia, and B. Alder
Phys. Rev. Lett. **74** 5212 (1995)

Measurements of the pressure in CBA are in very good agreement with hard sphere kinetic theory and molecular dynamics measurements.

Also get good results for the transport coefficients, namely viscosity, thermal conductivity, and diffusion coefficient.



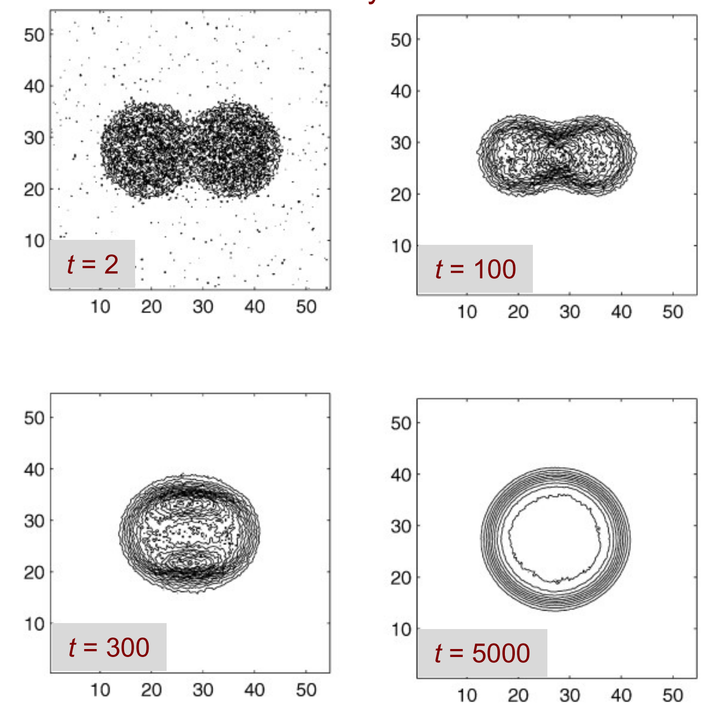
$n^* = n\, d^3$

Consistent Universal Boltzmann Algorithm (CUBA)

Making CBA displacement a function of density and temperature allows you to choose the equation of state.

Using van der Waals EoS we were able to simulate the condensation of vapor into liquid droplets.

Vapor condensation into a droplet
Density contours



F. Alexander, A. Garcia, and B.J. Alder, *Physica A* **240** 196 (1997)
A. Garcia, F. Alexander and B. Alder, *J. Stat. Phys.* **89** 403 (1997)
N. Hadjiconstantinou, A. Garcia, and B.J. Alder, *Physica A* **281** 337-47 (2000)

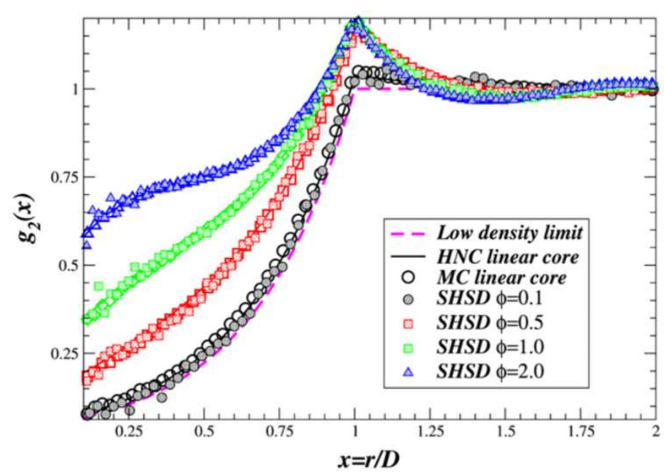
Enskog DSMC

CBA mantra:	Collisions affect particle positions
Enskog mantra:	Particle positions affect collisions

The most popular variants of DSMC for dense gases are based on the Enskog equation instead of the Boltzmann equation.

The correct virial Θ is obtained by having a collision probability that depends on both the relative velocity and the relative position for a particle pair.

Unlike CBA these can recover the correct pair correlation function in a dense gas.



A. Frezzotti, *Phys. Fluids* **9** 1329 (1997)
J. Montanero, A. Santos, *Phys. Fluids* **9** 2057(1997)
A. Donev, B. Alder, A. Garcia, *J. Stat. Mech.* **2009.11** P11008 (2009)

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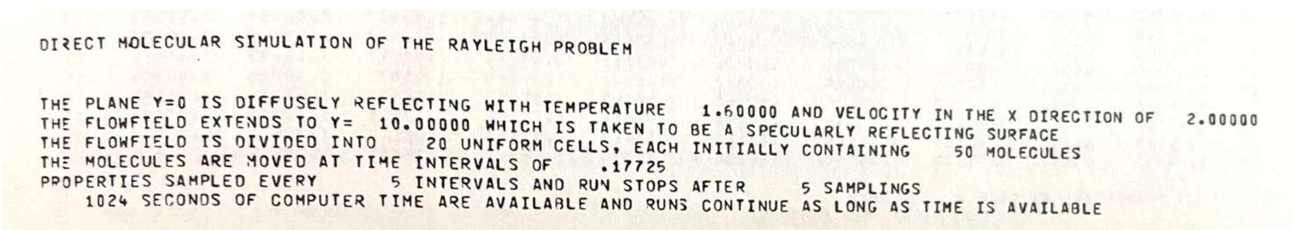
Cell size & Time step - 1976

In his first book Bird wrote:

“the results are remarkably insensitive … and no deleterious effects are generally present … if the cell size approaches the mean free path or if the time step approaches the mean collision time.”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DIRECT MOLECULAR SIMULATION OF THE RAYLEIGH PROBLEM

THE PLANE Y=0 IS DIFFUSELY REFLECTING WITH TEMPERATURE   1.60000 AND VELOCITY IN THE X DIRECTION OF   2.00000
THE FLOWFIELD EXTENDS TO Y=  10.00000 WHICH IS TAKEN TO BE A SPECULARLY REFLECTING SURFACE
THE FLOWFIELD IS DIVIDED INTO     20 UNIFORM CELLS, EACH INITIALLY CONTAINING    50 MOLECULES
THE MOLECULES ARE MOVED AT TIME INTERVALS OF     .17725
PROPERTIES SAMPLED EVERY      5 INTERVALS AND RUN STOPS AFTER     5 SAMPLINGS
    1024 SECONDS OF COMPUTER TIME ARE AVAILABLE AND RUNS CONTINUE AS LONG AS TIME IS AVAILABLE
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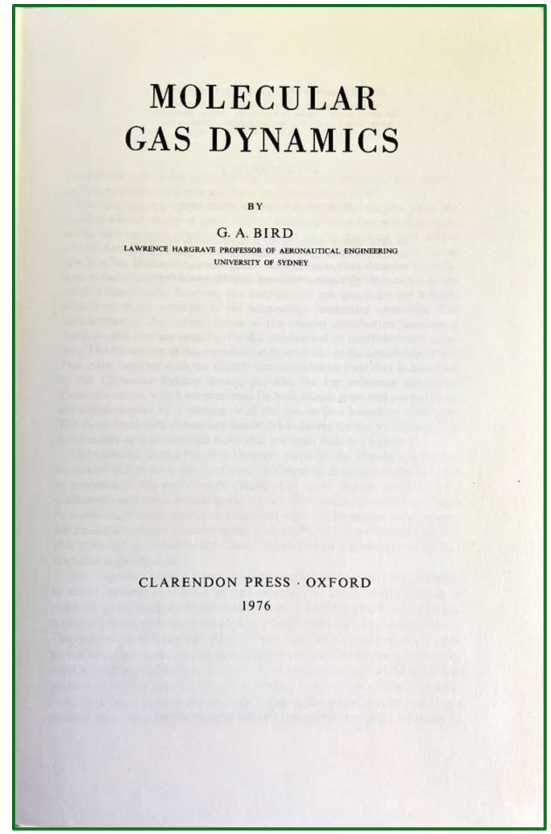
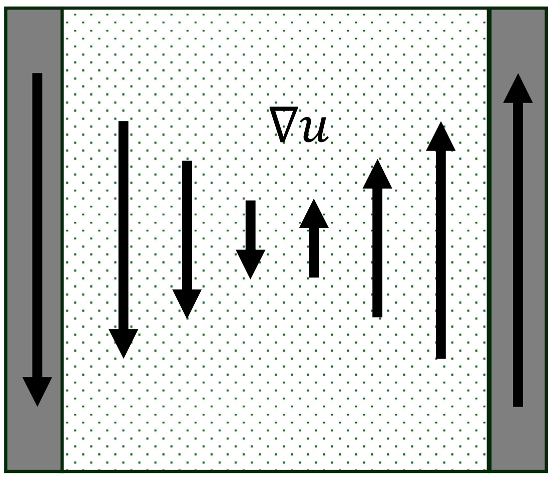
Program in his book sets collision cell size = ½ mean free path and time step = $^{1}/_{5}$ mean free time.

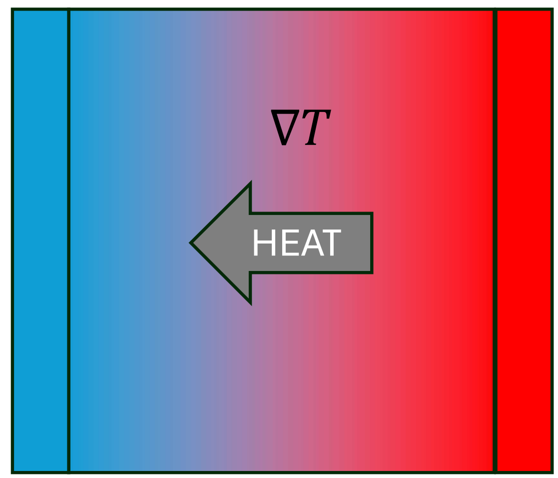


Testing Accuracy in DSMC

A way to quantify the error due to cell size and time step is to measure viscosity or thermal conductivity and compare with Chapman-Enskog theory (@ low Kn).



Couette Flow



Fourier Flow

G. A. Bird, M. A. Gallis, J. R. Torczynski, D. J. Rader, *Phys. Fluids* **21** 017103 (2009)

Measuring Transport in MD

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 53, NUMBER 10 15 NOVEMBER 1970

Studies in Molecular Dynamics. VIII. The Transport Coefficients for a Hard-Sphere Fluid*

B. J. ALDER, D. M. GASS, AND T. E. WAINWRIGHT

Lawrence Radiation Laboratory, University of California, Livermore, California

(Received 22 June 1970)

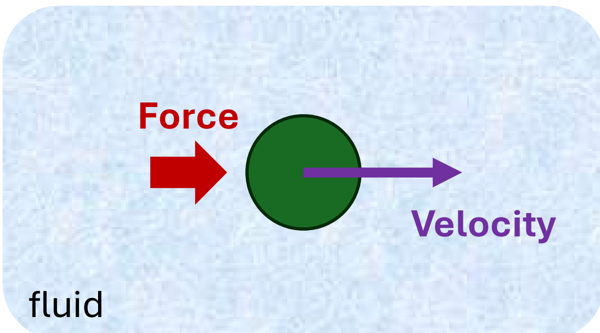
In the early days of Molecular Dynamics it was impossible to measure transport coefficients by applying a gradient (∇u or ∇T) because you could only run simulations containing a few hundred particles.

The results are primarily given for systems of 108 particles, but a few systems of 500 particles were studied

Einstein Theory for Brownian Motion

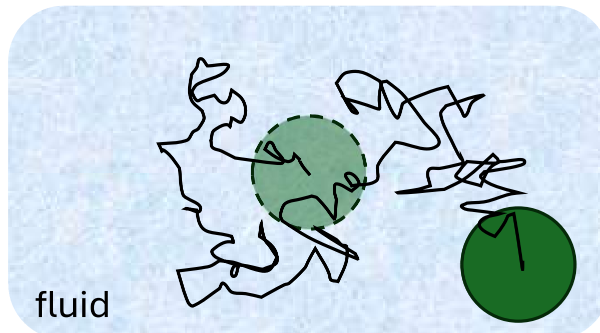
There are two ways to measure the mobility of a particle in a fluid.

Direct Approach



Mobility $\mu = \frac{v}{F}$

Brownian Motion Approach



Mobility $\mu = \frac{1}{6kT} \frac{\langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle}{t}$

Einstein's theory allows us to measure it at equilibrium (no applied force).

Viscosity: Einstein-Helfand Theory

We can measure viscosity of a fluid from molecule trajectories using Einstein-Helfand theory.

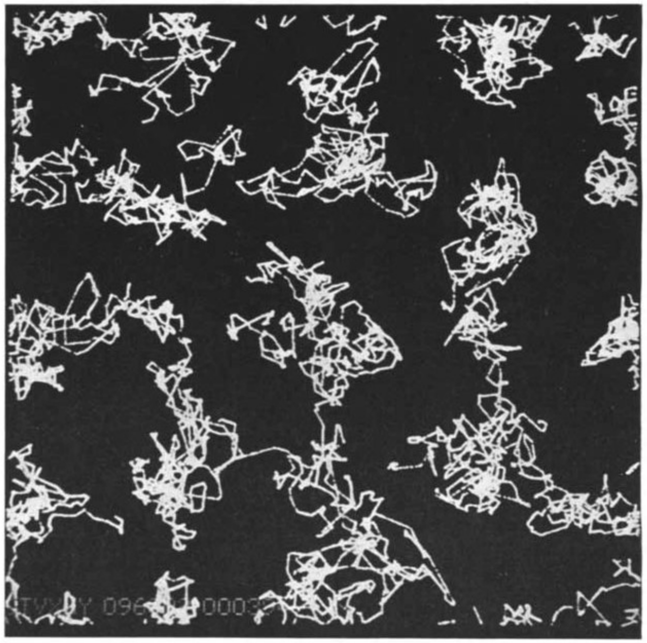
$$\eta = \frac{1}{2VkT} \frac{\langle [G(t) - G(0)]^2 \rangle}{t}$$

where

(*x*-velocity) x (*y*-position)

$$G(t) = m \sum_{i=1}^{N} \dot{x}_i(t) y_i(t)$$

This allows us to measure viscosity (and other transport coefficients) from *equilibrium* simulations.



Fluctuation-Dissipation Theorem

Viscosity: Green-Kubo Theory

A related approach uses the off-diagonal stress tensor component,

$$J(t) = \dot{G}(t) = m\sum_{i=1}^{N} \dot{x}_i(t)\dot{y}_i(t) + \tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} F_{ij}^{x}(t)\left(y_i - y_j\right)$$

where $\vec{F}_{ij}$ is the force between molecules, and writes the previous result as,

$$\eta = \frac{1}{VkT}\int_0^\infty \langle J(t)\, J(0)\rangle\, dt \qquad \text{(Green-Kubo)}$$

Notice that $J = J^K + J^C$, so it is the sum of a kinetic (ballistic) contribution and a contribution due to transfer of momentum by intermolecular forces.

Viscosity: Wainwright calculation

By writing the hard sphere collisional contribution as

$$J(t) = m \sum_{i=1}^{N} \dot{x}_i(t)\dot{y}_i(t) + \sum_{collisions} \frac{m}{d^2} \left(\Delta\vec{\boldsymbol{v}}_\alpha \cdot \vec{\boldsymbol{r}}_{\alpha\beta}\right)\left(x_\alpha - x_\beta\right)\left(y_\alpha - y_\beta\right)\ \delta(t - t_c)$$

t_c : time of collision

Wainwright was able to evaluate the integrations to obtain

$$\eta = \frac{1}{VkT}\int_0^\infty \langle\, J(t)\, J(0)\rangle\, dt = \ \eta^K + \eta^{K\times C} + \eta^C$$

T. Wainwright, *J. Chem. Phys.* **40** 2932 (1964)

The kinetic contribution η^K is precisely the Chapman-Enskog viscosity. The cross term $\eta^{K\times C}$ and the collision term η^C are dense gas corrections.

In DSMC the collision term η^C is ***not*** zero because of the finite distance between collision partners (i.e., finite collision cell size).

DSMC Cell Size Error

For DSMC with collision rate Γ we have

$$\eta^C = \frac{m^2\Gamma}{2kT}\left\langle\left(y_\alpha - y_\beta\right)^2\right\rangle \underbrace{\left\langle\left(\Delta\dot{x}_\alpha - \Delta\dot{x}_\beta\right)^2\right\rangle}_{= 4kT/3m}$$

For cubic cells

$$\left\langle\left(y_\alpha - y_\beta\right)^2\right\rangle = \frac{\ell^2}{6}$$

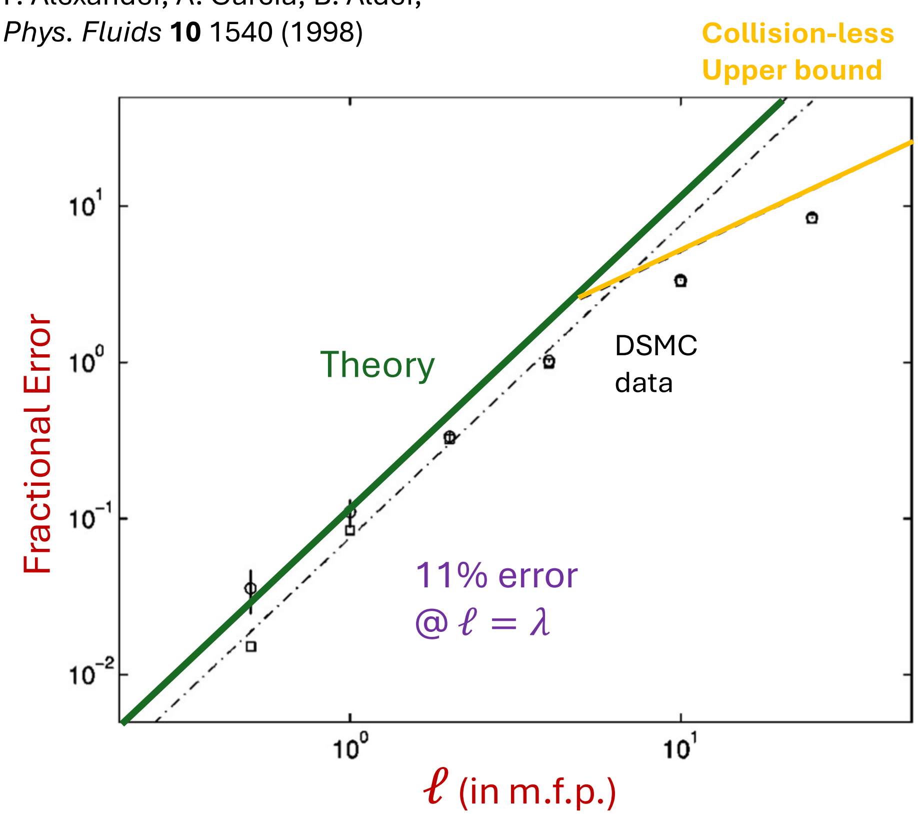
ℓ: cell size

Net viscosity $(\eta^K + \eta^C)$ is

$$\eta = \frac{5}{16\, d^2}\sqrt{\frac{mkT}{\pi}}\left(1 + \frac{16}{45\,\pi}\frac{\ell^2}{\lambda^2}\right)$$

In DSMC $\eta^{K\times C} = 0$

F. Alexander, A. Garcia, B. Alder, *Phys. Fluids* **10** 1540 (1998)



Similar results for thermal conductivity

DSMC Time Step Error

N. Hadjiconstantinou, *Phys. Fluids* **12** 2634 (2000)
A. Garcia, W. Wagner, *Phys. Fluids* **12**, 2621 (2000)

Hadjiconstantiou showed that even in the limit of small collision cells ($\ell \to 0$) there is a non-zero contribution to η^C because the collision happens at the *wrong time*.

For a DSMC time step of τ

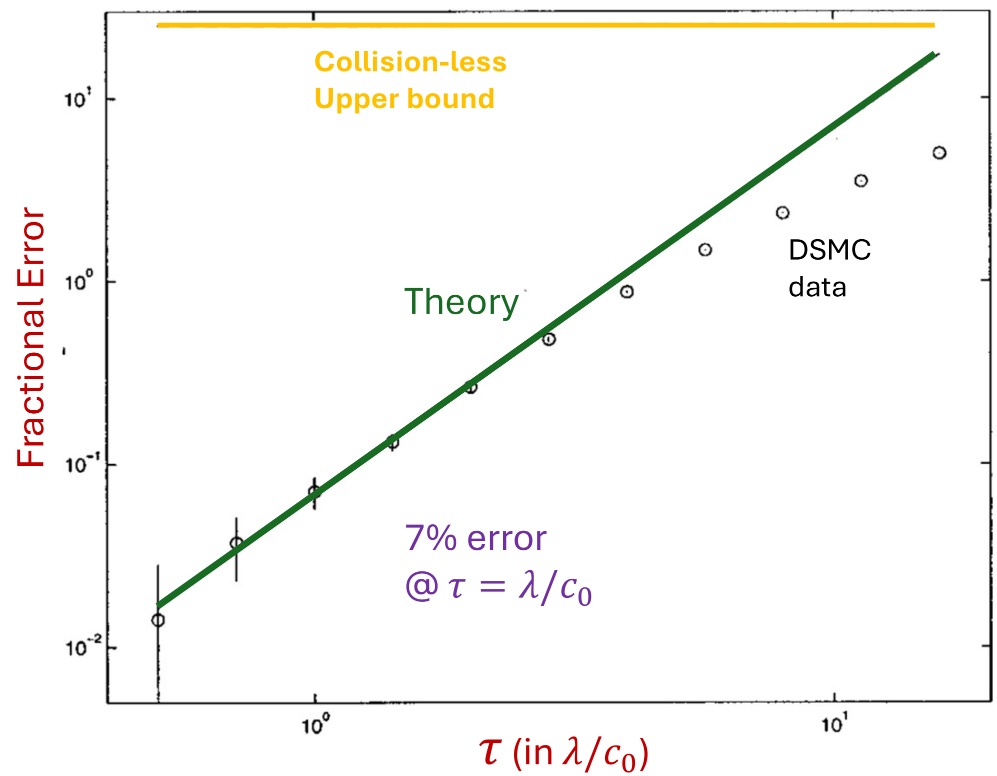
$$y_\alpha - y_\beta = \left(t_c - \tfrac{1}{2}\tau\right)\left(\dot{y}_\alpha - \dot{y}_\beta\right)$$

Net viscosity $(\eta^K + \eta^C)$ is

$$c_0 = \sqrt{2kT/m}$$

$$\eta = \frac{5}{16\, d^2}\sqrt{\frac{mkT}{\pi}}\left(1 + \frac{32}{150\,\pi}\,\frac{c_0^2\tau^2}{\lambda^2}\right)$$

Again, in DSMC $\eta^{K\times C} = 0$



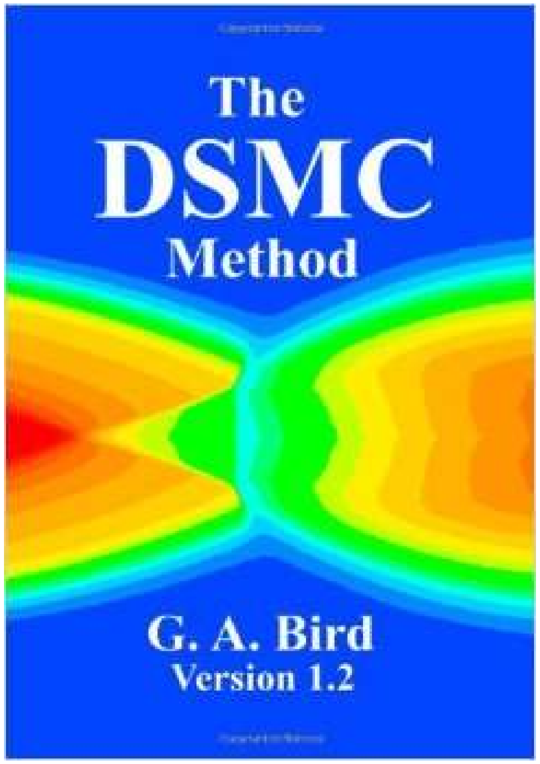
Similar results for thermal conductivity and diffusion

Cell size & Time step - 2013

In his last book, Graeme wrote,

“Early DSMC programs…the mean spacing between collision pairs was too large in comparison with the mean free path and this led to the introduction of sub-cells…(and) an option to select the collision pairs from the nearest-neighbour pairs within the cell.”

“The time step is set to a specified small fraction of the sampled mean collision time…”



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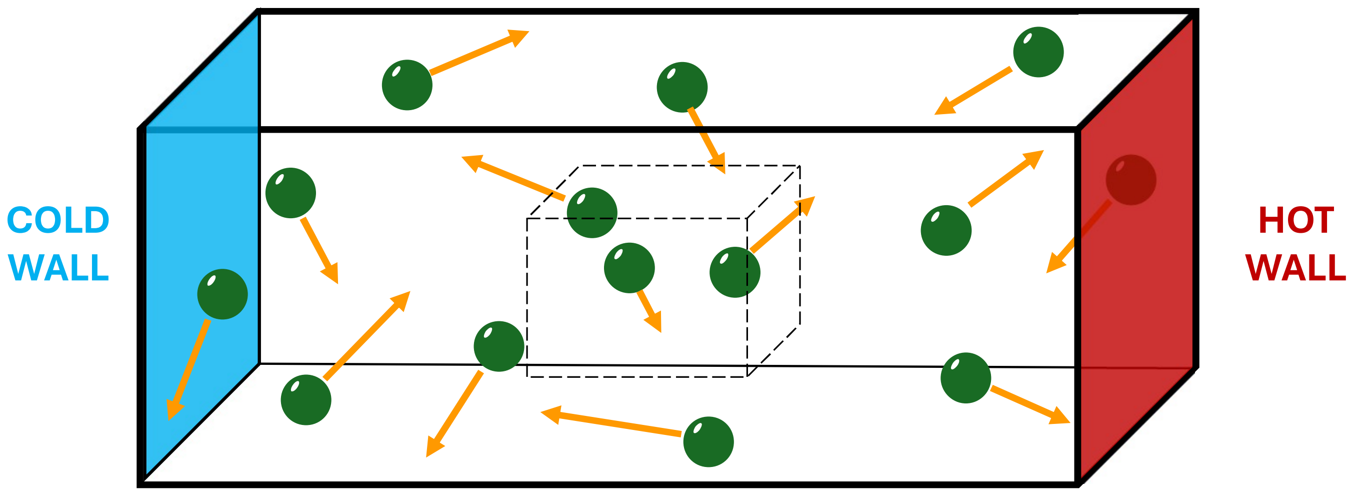
Hydrodynamic Fluctuations



My original interest in DSMC was to study fluctuations

$$\delta\rho(x,t) = \rho(x,t) - \langle\rho(x)\rangle$$

(Density fluctuation) = (Density) – (Average Density)

Fluctuations & DSMC - 1976

In his first book Bird describes fluctuations as an unavoidable annoyance inherent with DSMC.

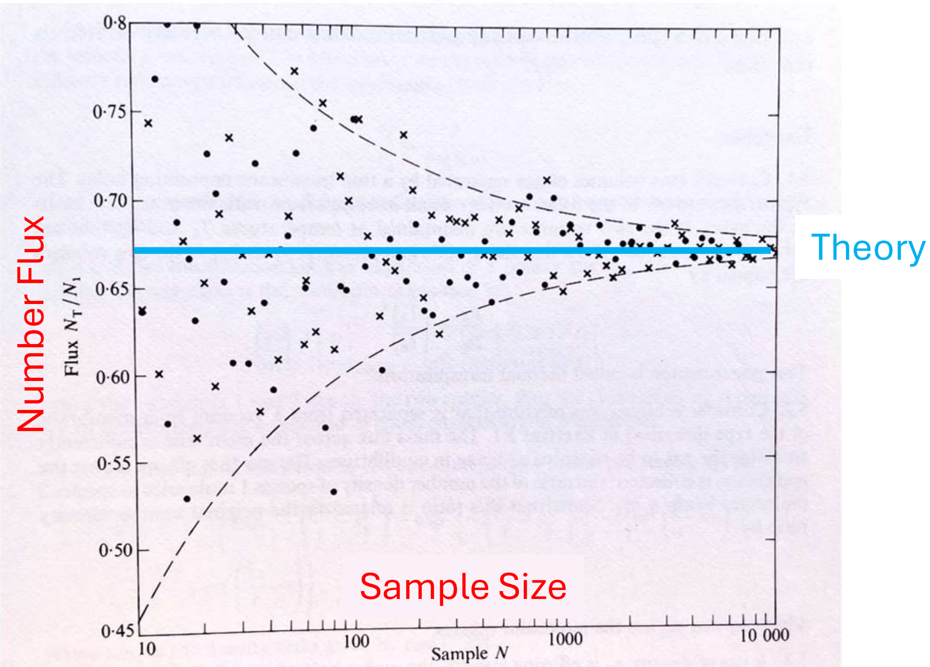
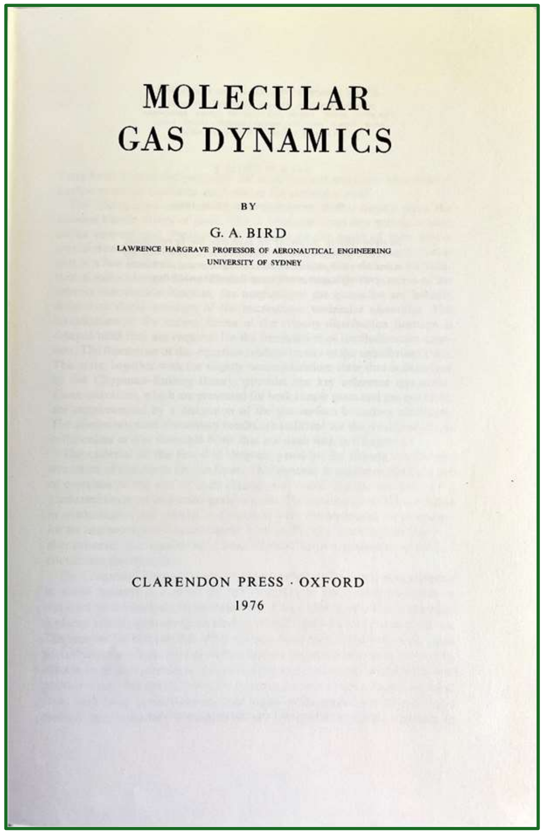


FIG. 5.8. Effect of sample size on the scatter in a typical Monte Carlo result ($L = 1$).

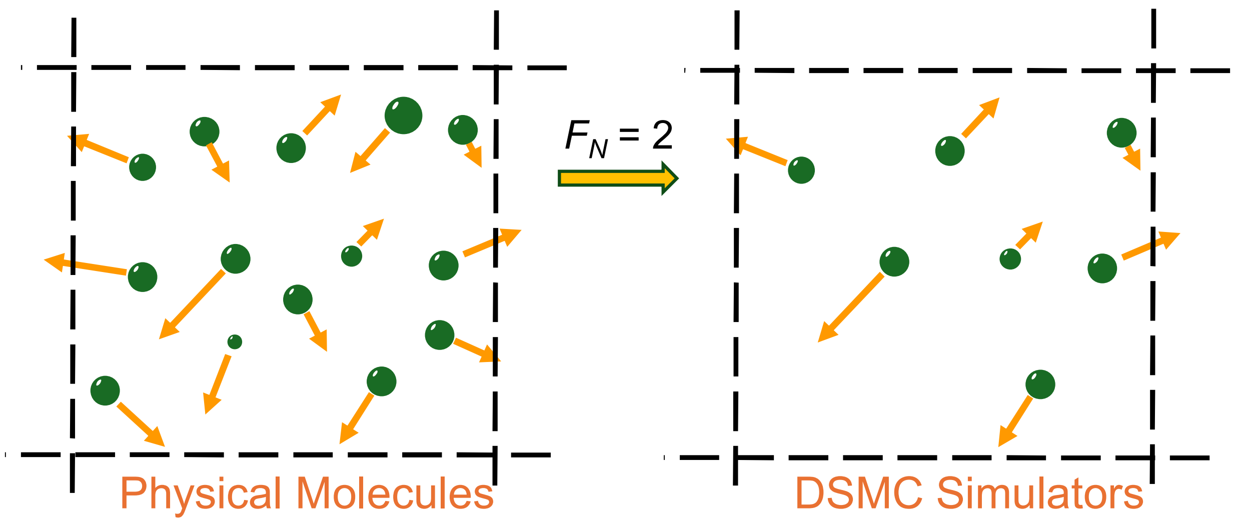


Fluctuations are NOT due to Monte Carlo collisions

Molecules vs. “Simulators”

In DSMC the number particles (“simulators”) is a small fraction of the number of physical molecules.

Each DSMC simulator represents F_N physical molecules.
Each DSMC collision represents F_N physical collisions.



DSMC fluctuations are physical fluctuations only magnified by F_N .

Statistical Error Estimates

Statistical mechanics tells us the standard deviation of hydrodynamic variables, allowing us to estimate statistical error in particle simulations.

For example, when estimating the average fluid velocity in a cell with ***N* simulators**, the fractional error in the x-component is expected to be

$$E_u = \frac{\sigma_u}{|u_x|} = \frac{\sqrt{\langle \delta u_x^2 \rangle} / \sqrt{S}}{|u_x|} \approx \frac{1}{\sqrt{SN}} \frac{1}{\mathrm{Ma}}$$

From statistical mechanics

$$\langle \delta u_x^2 \rangle = \frac{kT}{mN}$$

where *S* is number of samples, Ma is Mach number.

N. Hadjiconstantinou, A. Garcia, M. Bazant, G. He, *J. Comp. Phys.* **187** 274-297 (2003)

Statistical Error Estimates (cont.)

For fractional error in fluid velocity of E_u = 1% with N = 100 simulators/cell

$$S \approx \frac{1}{N \mathrm{Ma}^2 E_u^2} \propto \frac{1}{\mathrm{Ma}^2}$$

$S \approx 10^2$ samples for Ma =1.0 (Aerospace flow)
$S \approx 10^8$ samples for Ma = 0.001 (Microscale flow)

Fractional error in density, temperature, pressure

$$E_\rho = \frac{1}{\sqrt{SN}} \qquad E_T = \frac{C}{\sqrt{SN}} \qquad E_P = \frac{C'}{\sqrt{SN}} \qquad C, C' = O(1)$$

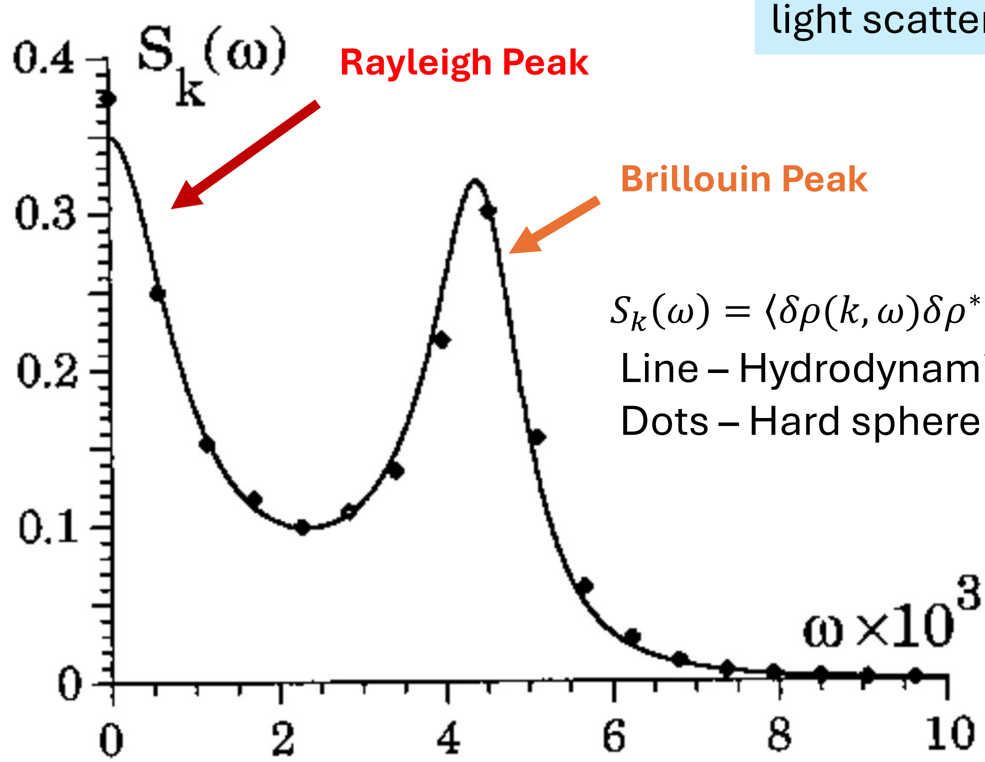
All the error estimates are the *same* for DSMC and MD.

N. Hadjiconstantinou, A. Garcia, M. Bazant, G. He,
J. Comp. Phys. **187** 274-297 (2003)

Dynamic Structure Factor

Experimentally measureable by light scattering

Measuring the time-space correlations of density fluctuations at equilibrium yields hydrodynamic information, such as sound speed and viscosity.



$S_k(\omega) = \langle \delta\rho(k,\omega)\delta\rho^*(k,\omega)\rangle$

Line – Hydrodynamics

Dots – Hard sphere DSMC

F. Baras, M. Malek Mansour, A. Garcia, M. Mareschal, *J. Comp. Phys*. **119** 94 (1995).

Dynamic Structure Factor (cont.)

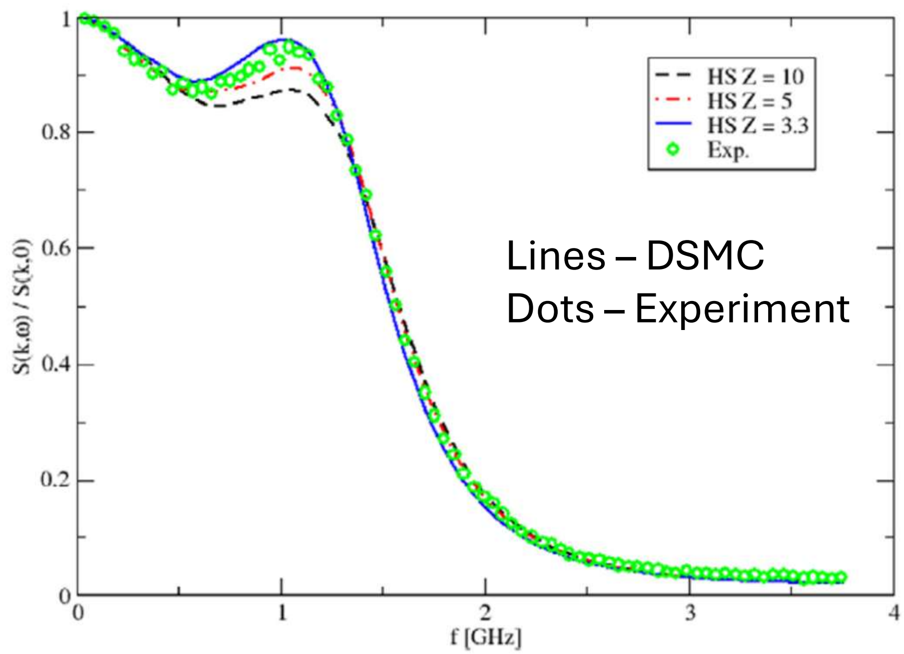


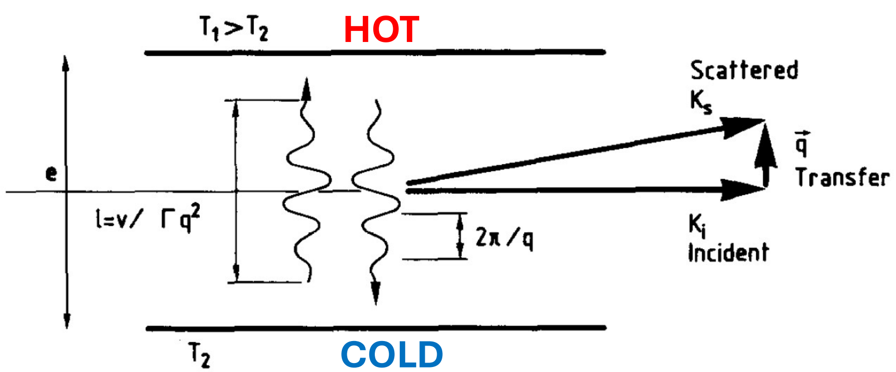
Fig. 2. Comparison of experimental and calculated RBS spectra for $p = 3.419$ bar, $T = 339.1$ K. DSMC results are obtained with the HS-LB model with different values for the rotational relaxation number.

The dynamic structure factor,
$S(k,\omega) = \langle \delta\rho(k,\omega)\delta\rho^*(k,\omega)\rangle$,
at equilibrium is a useful way to compare DSMC models (e.g., rotational relaxation) with data from scattering experiments and with theoretical predictions.

D. Bruno, A. Frezzotti, G. P. Ghiroldi, *Eur. J. Mech. B (Fluids)*, **64** 8 (2017)
D. Bruno, V. Giovangigli, *Fluids* **7** 356 (2022)

Fluctuations in a Temperature Gradient

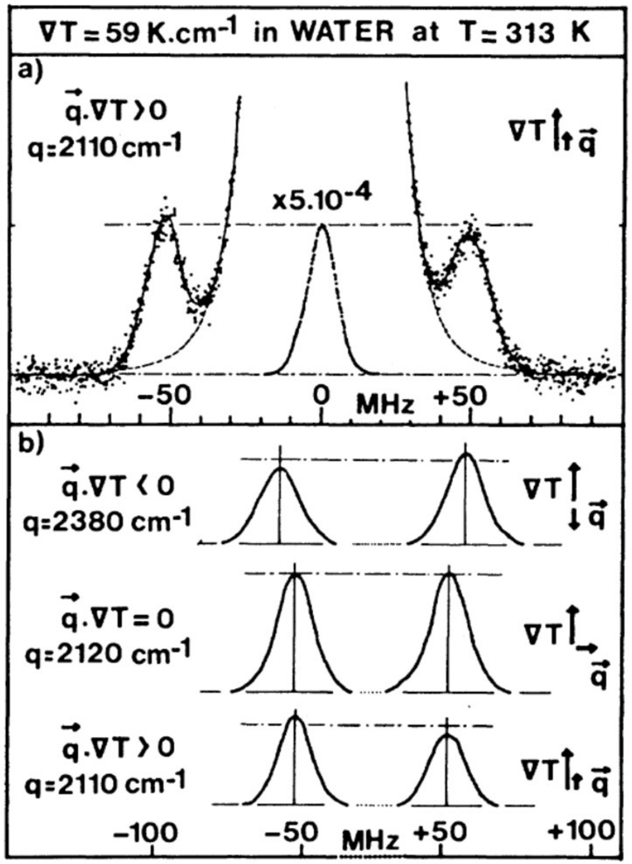
In the 1980's light scattering experiments confirmed theoretical predictions that random pressure fluctuations (sound waves) are asymmetric when $\nabla T \neq 0$.



Attempts to measure this phenomenon by Molecular Dynamics had mixed success.

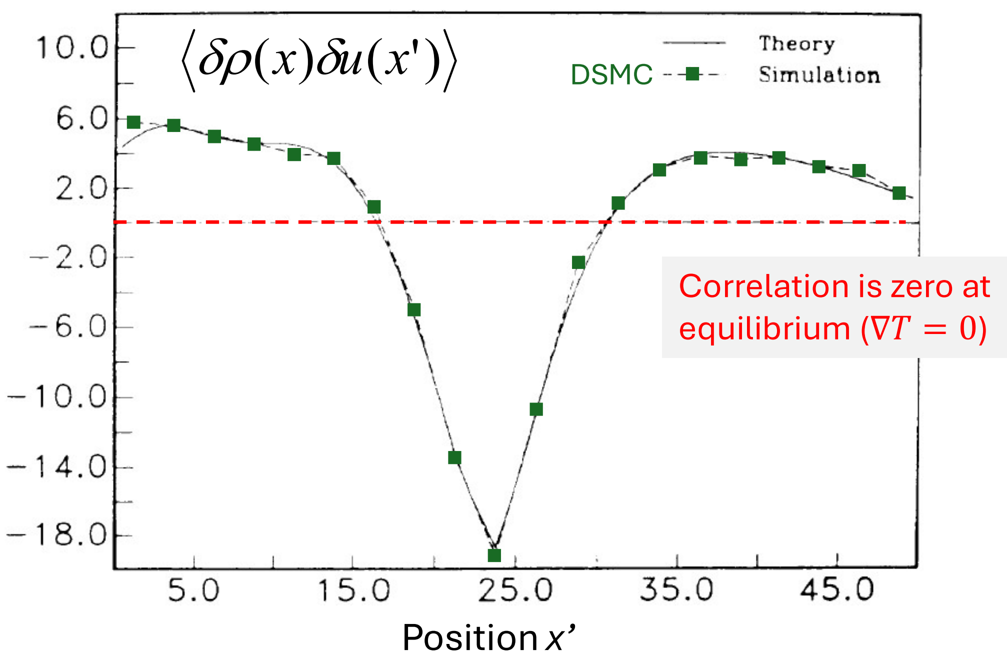
M. Mareschal , E. Kestemont, *Phys. Rev. A* **30**, 1158 (1984)

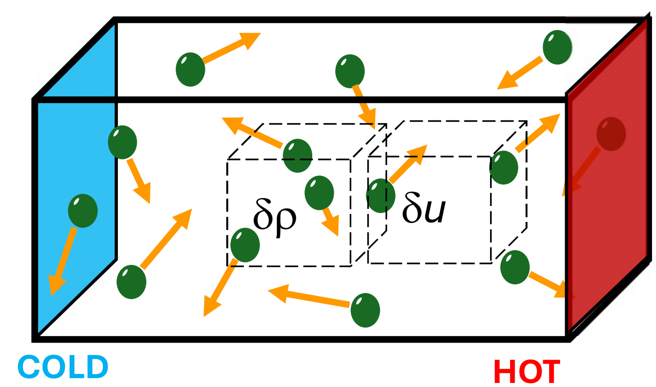
D. Beysens, *Physica A* **118**, 250-267 (1983)



Density-Velocity Correlation

DSMC simulations were in perfect agreement with the theoretical prediction of a correlation in density-velocity fluctuations under ∇T

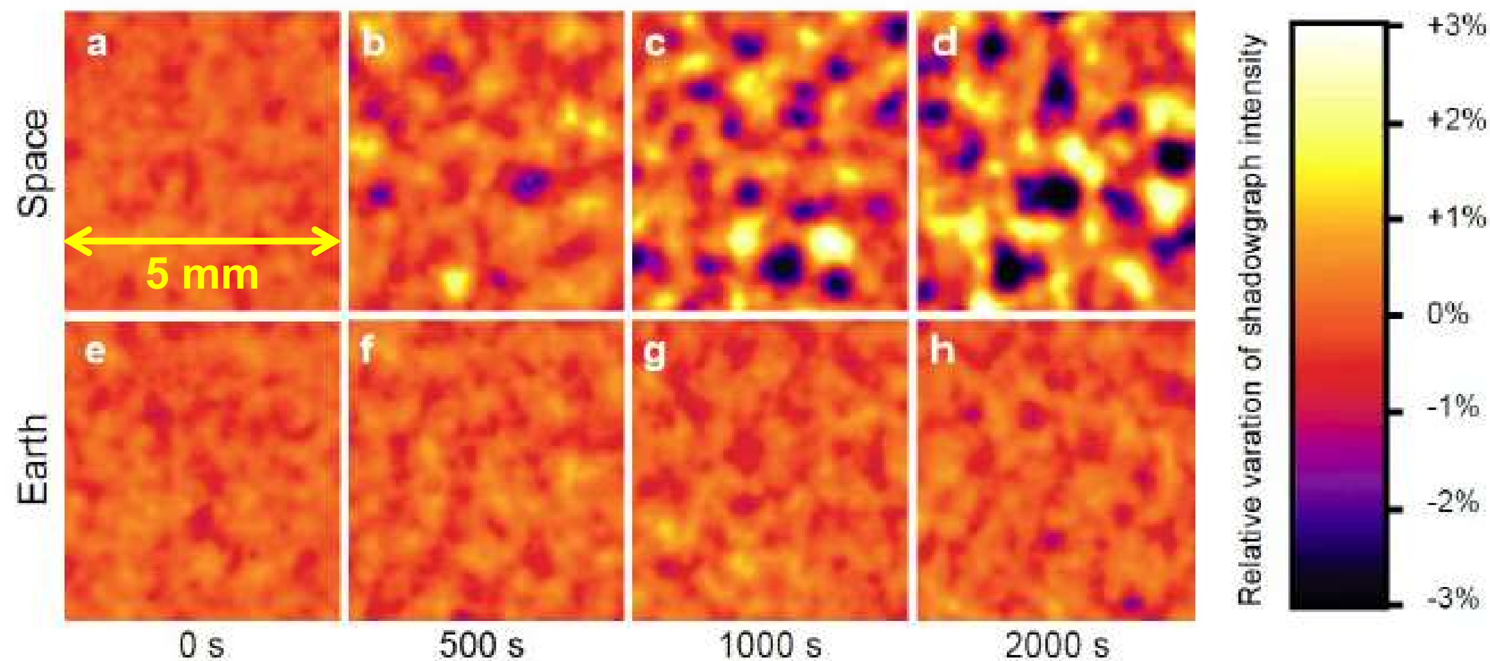


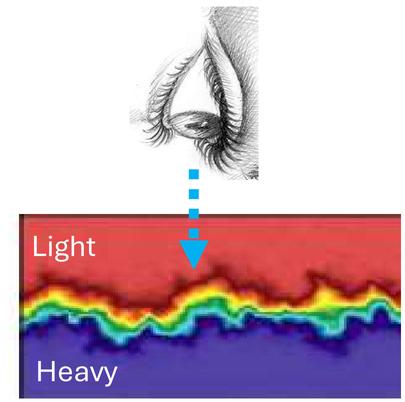


A. Garcia, *Phys. Rev. A* **34** 1454 (1986)

Giant Fluctuation Phenomenon

Vailati, et al., *Nature Comm.*, **2** (2011)



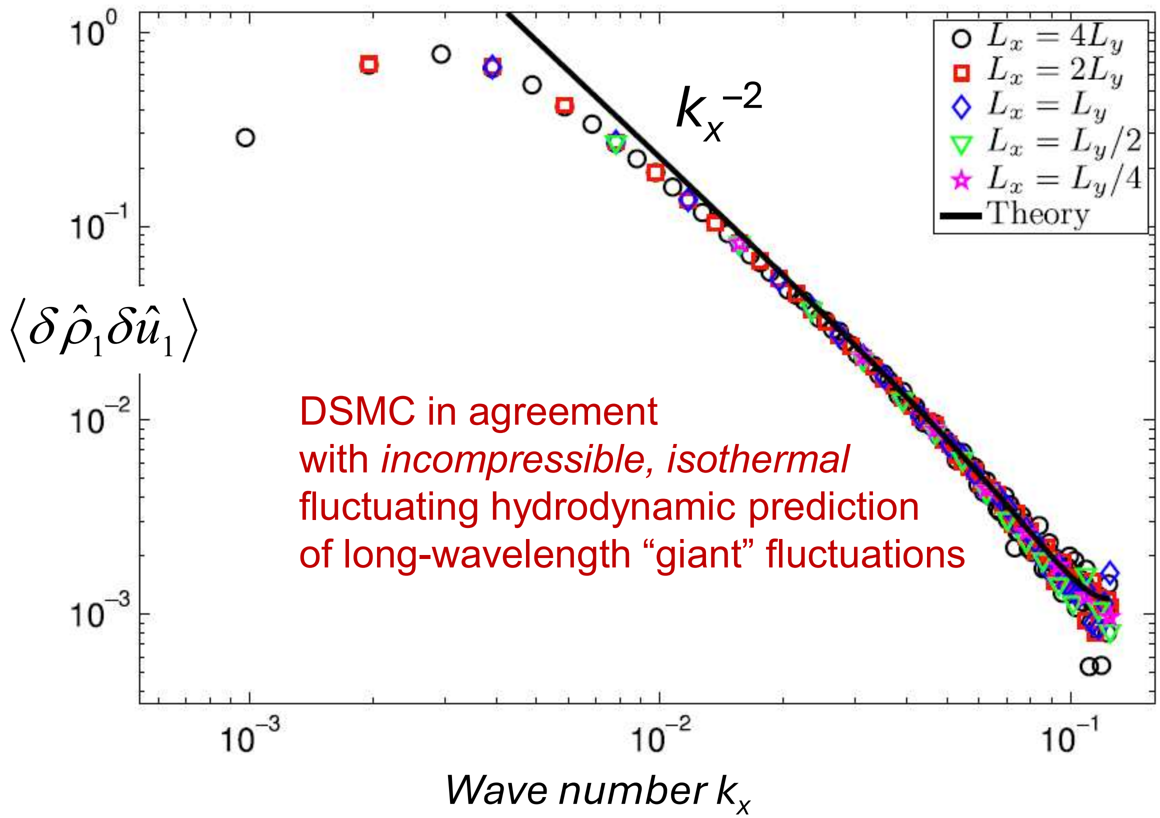


Top-down view of density fluctuations during mixing

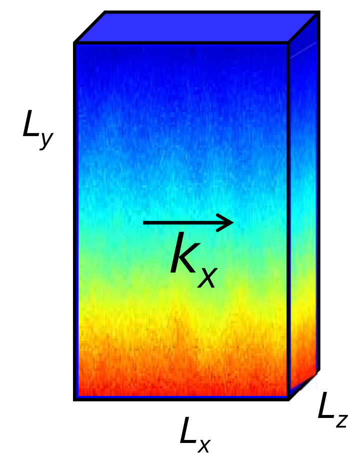
Experiments in 2011 found *macroscopic* fluctuations in interface mixing.
Phenomenon due to correlation of concentration-velocity fluctuations.

Concentration-Velocity Correlation

A. Donev, A. Garcia, A. de la Fuente, J. Bell,
J. Stat. Mech. 2011:P06014 (2011)

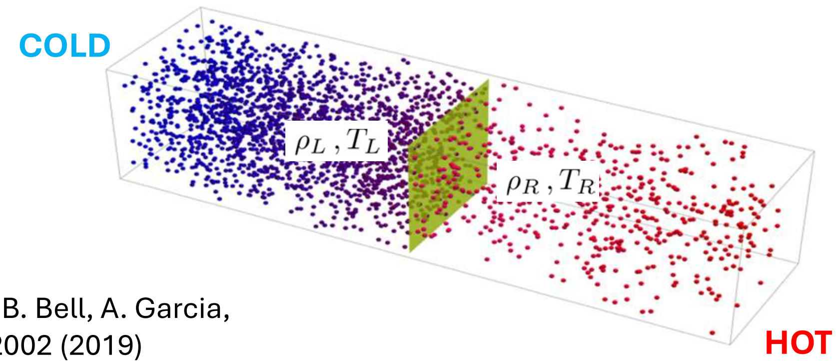


Symbols are DSMC;
$k_y = 0$

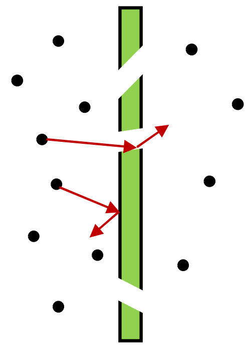


$L_y = 512\,\lambda$; $L_z = 2\,\lambda$

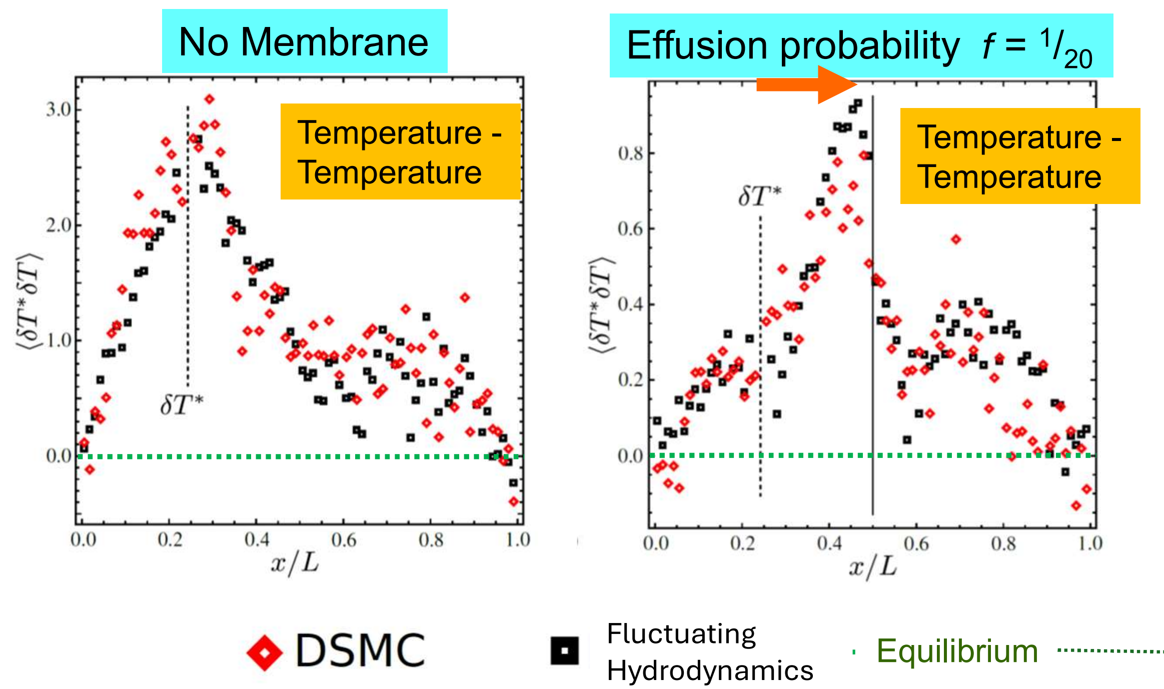
Fluctuations & Membranes



Molecules reaching the interface cross it with probability *f*.



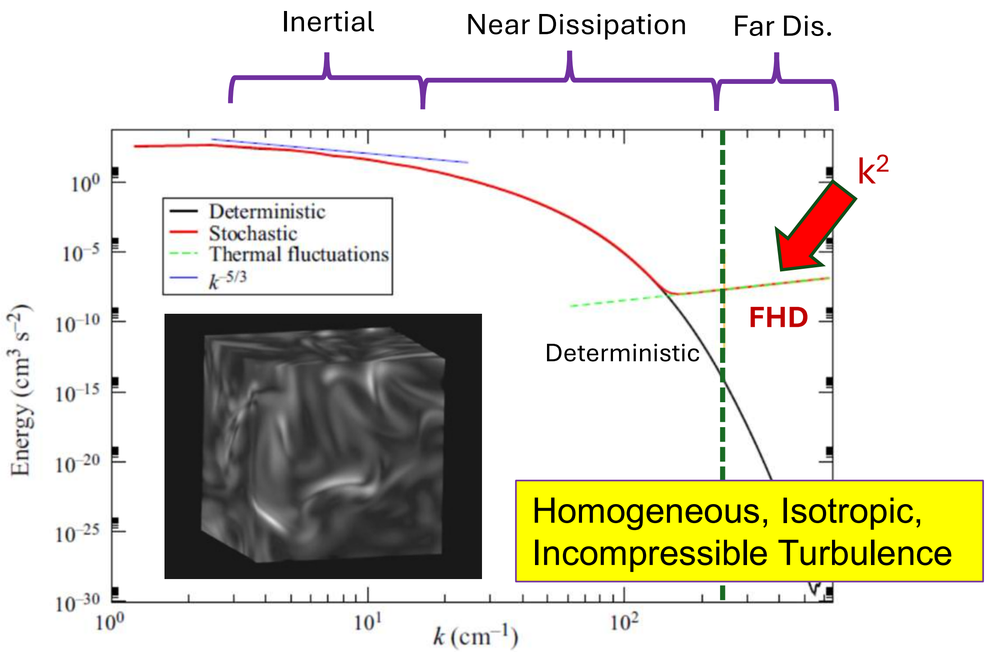
D. Ladiges, A. Nonaka, J.B. Bell, A. Garcia, *Physics of Fluids* **31**, 052002 (2019)



Temperature-temperature correlation is reduced but shifted by an effusion membrane in the center.

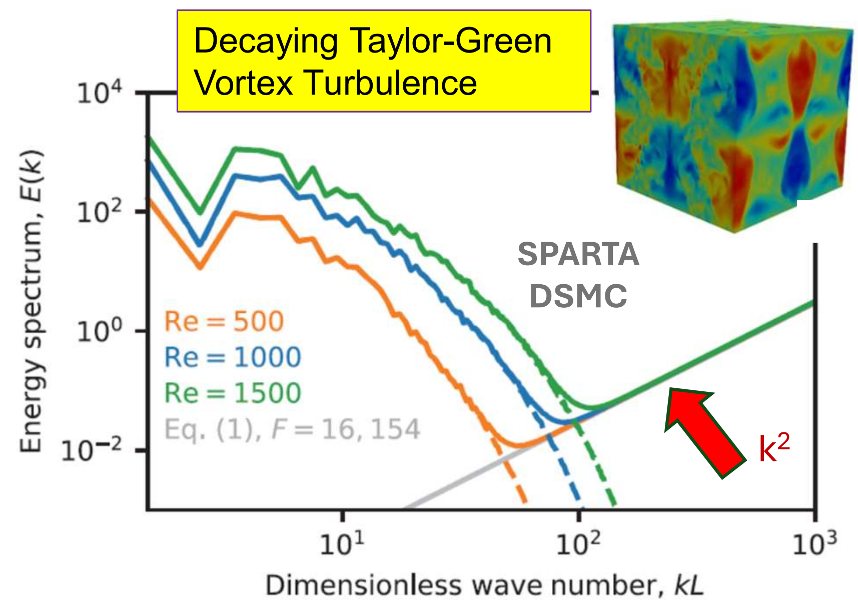
Fluctuations & Turbulence

Thermal fluctuations dominate turbulent fluctuations in the near-dissipation range



Using Fluctuating Hydrodynamics (FHD)

J. Bell, A. Nonaka, A. Garcia, G. Eyink,
J. Fluid Mech. **939** A12 (2022)



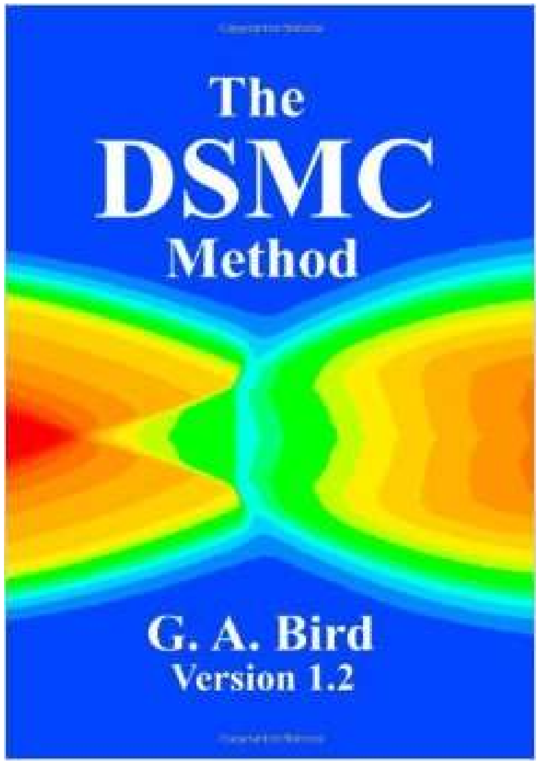
Using Sparta DSMC

R. McMullen, M. Krygier, J. Torczynski, M. Gallis,
Phys. Rev. Lett. **128** 114501 (2022)

Fluctuations & DSMC - 2013

In his last book, Graeme wrote,

"While the fluctuations are unphysical when F_N is large, they are physically realistic ... (with) a one-to-one correspondence between real and simulated molecules. This is another instance of DSMC going beyond the Boltzmann equation because fluctuations are neglected in the Boltzmann model."



His last 3 papers were on Brownian motion.

Nano energy **11**, 463-470 (2015); *Phys. Fluids* **28** 062005 (2016); *NanoWorld* **3** 18 (2018)

Five Short Stories

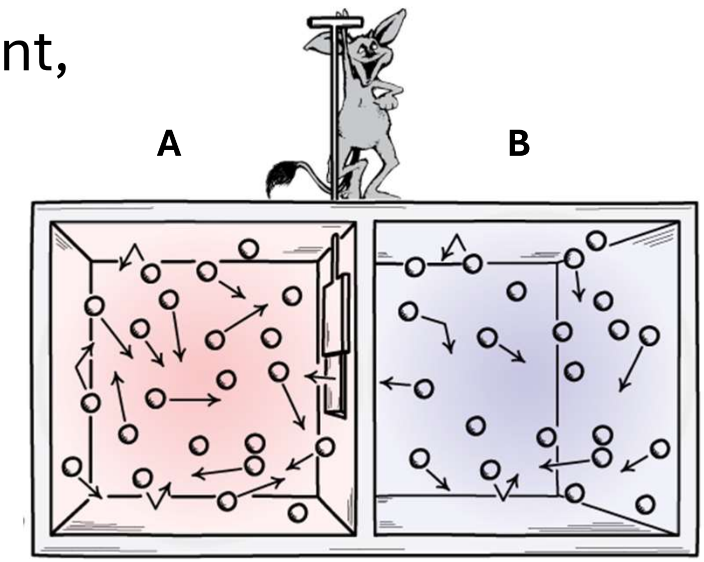
This talk describes Direct Simulation Monte Carlo as viewed from the perspective of statistical mechanics.

- DSMC & Molecular Dynamics – Brothers separated at birth
- DSMC equation of state – Why ideal gas law?
- Transport in DSMC – A lesson from Molecular Dynamics
- Statistical fluctuations – One man's garbage…
- Second Law of Thermodynamics – Exorcising the demons

Maxwell's Demon

DSMC is such a being!

In 1887 Maxwell presented a thought experiment,



"… conceive of a being whose faculties are so sharpened that he can follow every molecule in its course…

so as to allow only the swifter molecules to pass from A to B, and only the slower molecules to pass from B to A.

He will thus, without expenditure of work, raise the temperature of B and lower that of A, in *contradiction to the second law of thermodynamics*."

Demons in DSMC ?

The DSMC algorithm has full information and control of the particles' dynamics and has many complex stages

- Collision rate (Time counter, NTC, Bernoulli trials, ...)
- Basic collisions (VHS, VSS, Lennard-Jones models, ...)
- Complex collisions (Internal energy, chemistry models, ...)
- Particle motion (External fields, Adaptive time step, ...)
- Boundary conditions (Surface models, Inflow/Outflow, ...)

How can we be sure that a flawed design or a "bug" has not introduced a Maxwell demon into our simulations?

Second Law of Thermodynamics

How do we test that our simulations satisfy the Second Law?

Boltzmann's H-theorem is *not* useful since, due to fluctuations, DSMC satisfies it only in the limit of infinite number of particles.

Stochastic thermodynamic identities, such as Crooks fluctuation theorem, could be tested in principle but in practice they are difficult to verify in simulations.

Detailed Balance & Reversibility

Detailed balance is a necessary condition for microscopic reversibility, which is a sufficient condition for an algorithm to obey the Second Law.

J.S. Thomsen, *Phys Rev.* **91** 1263 (1953)

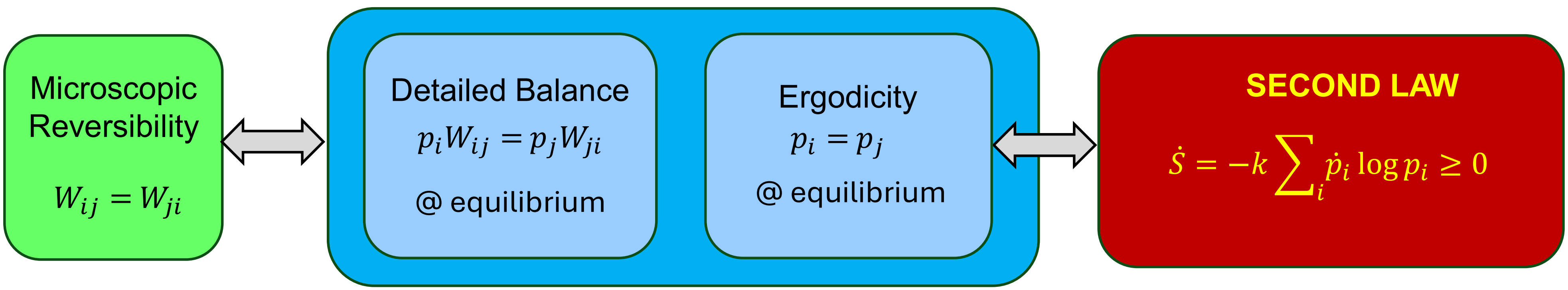
For an isolated system with microstate dynamics

$$\dot{p}_i = \sum_j (p_j W_{ji} - p_i W_{ij})$$

$\dot{p}_i = 0$ @ equilibrium

p_i: Probability of state i

W_{ij}: Transition rate $i \to j$



Cercignani–Lampis surface scattering model

Cercignani and Lampis formulated a surface scattering model based on the requirement of detailed balance; popularized in DSMC by Lord.

Since the laws of both classical and quantum mechanics determine uniquely the final state once the initial state is known, and are time reversible, the final state also determines uniquely the initial state; then,

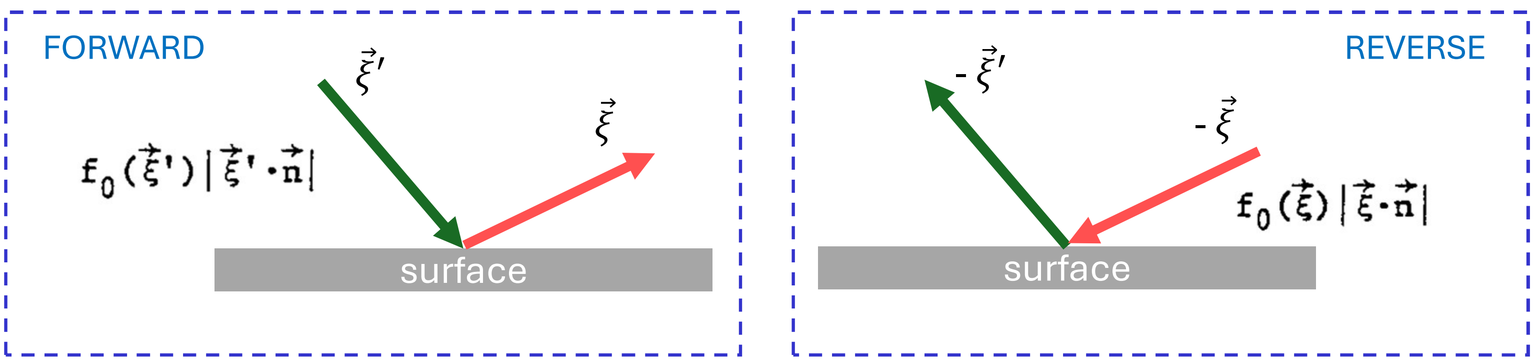
* * *

becomes the following equation, expressing a detailed balancing at the wall:

$$R(\vec{\xi}' \to \vec{\xi})\, f_0(\vec{\xi}')|\vec{\xi}'\cdot\vec{n}| = R(-\vec{\xi} \to -\vec{\xi}')\, f_0(\vec{\xi})|\vec{\xi}\cdot\vec{n}|, \quad (\vec{\xi}'\cdot\vec{n} < 0,\ \vec{\xi}\cdot\vec{n} > 0)$$

$$W_{ij}\, p_i = W_{ji}\, p_j$$

C. Cercignani and M. Lampis, *Trans. theory & stat. phys.*, ***1*(2)**, 101-114. (1971)



Ergodicity & Fluctuations

One way to test any molecular code for ergodicity at equilibrium is to measure fluctuations and compare with statistical mechanics.

For example, for cells i and j

A. Garcia, *CAMCoS* **1** 53-78 (2006)

$$\langle \delta\rho_i \delta u_j \rangle = 0 \qquad \text{and} \qquad \langle \delta u_i \delta u_j \rangle = \frac{k\langle T_i \rangle}{m\langle N_i \rangle}\delta_{i,j}$$

with similar expressions for others, such as $\langle \delta\rho_i \delta T_j \rangle$, $\langle \delta u_i \delta T_j \rangle$, etc.

Results should be *independent* of internal molecular processes (e.g., vibrational exchange) and of any chemical processes.

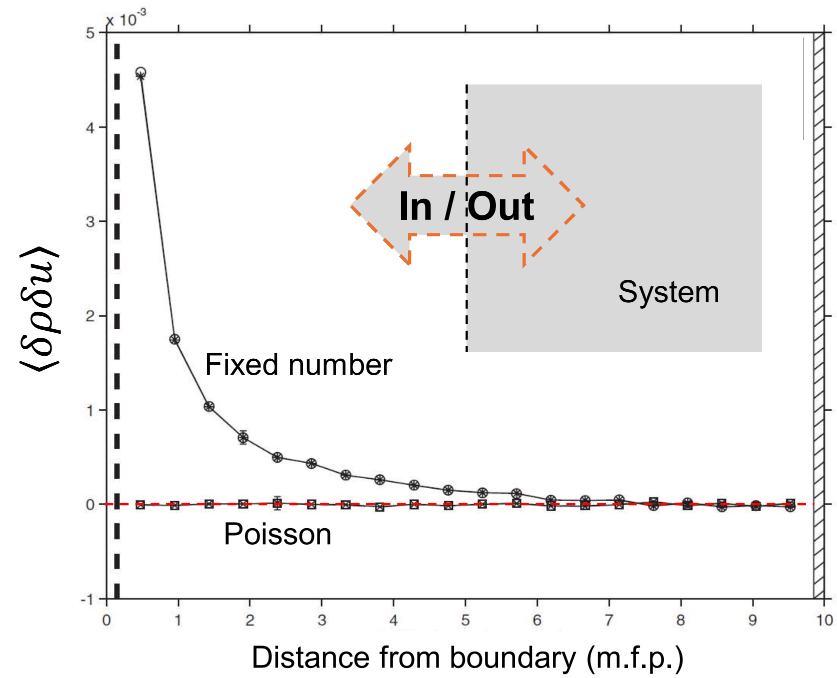
Many DSMC codes will *not* pass this test!

Inflow / Outflow Boundary

M. Tysanner A. Garcia,
Int. J. Num. Meth. Fluids **48** 1337 (2005)

An inflow / outflow boundary models an infinite reservoir of particles with an equilibrium density and temperature.

Number of particles generated at the boundary must be Poisson distributed for detailed balance.



Generation not Poissonian → No Detailed Balance → *Ergodic @ equilibrium?* ← **NO** ← $\langle \delta\rho\delta u \rangle \neq 0$

A New Age: AI / ML

The capabilities of Artificial Intelligence / Machine Learning systems are growing exponentially thanks to the availability of massive data sets.

ChatGPT (launched 2022)

You
What is Direct Simulation Monte Carlo?

ChatGPT
Direct Simulation Monte Carlo (DSMC) is a computational technique used to simulate the behavior of rarefied gas flows, where the mean free path of gas molecules is comparable to or larger than the characteristic length of the flow. This makes traditional continuum fluid dynamics models less accurate, and DSMC becomes more suitable.

Here's how DSMC works:

1. **Particle-Based Simulation:** DSMC simulates the gas flow by modeling the behavior of individual gas molecules (or small groups of molecul... called particles) rather than using a continuous

Nature (November 2023)

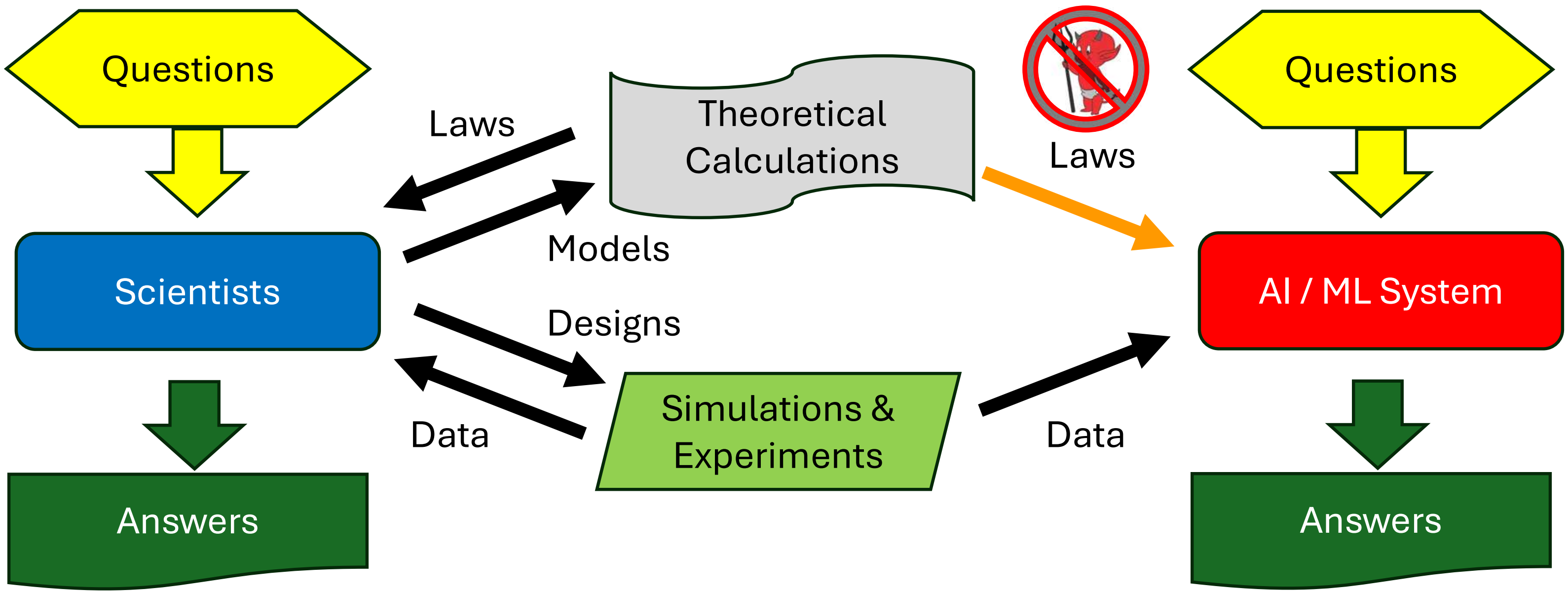
DeepMind AI accurately forecasts weather – on a desktop computer

The machine-learning model takes less than a minute to predict future weather worldwide more precisely than other approaches.

ML session tomorrow morning

	10 **Machine Learning** Chair: C. Tantos
10:50	**R. Martin** Data-Driven Extraction of 3D Orthogonal Velocity Distribution Modes from 1D DSMC Shocks
11:10	**D. Valougeorgis** Advancing neutral gas exhaust modeling in fusion reactors by machine learning techniques
11:30	**D. Waidmann** Deep learning closure of the Navier–Stokes equations for hypersonic transition-continuum flows using implicit-in-time adjoint optimization
11:50	**J. Tucny** Physics-informed neural networks to learn the impact of curvature on rarefied gas flow characteristics
12:10	**N. Daultry Ball** Direct Molecular Simulation of 1D Normal Shock Waves with a Neural Network Collision Model

Science in the AI / ML Age



How can physical laws be "guard rails" without stifling the creativity of AI / ML systems?

Thank you for your attention and participation

Have a wonderful RGD!

Graeme Bird