General Features of Our Approach to NESM & NEMD

Our main goal is to reach an understanding connecting microscopic and mesoscopic models to analogs in the Real World of Macroscopic Physical Phenomena . We strive for simplicity . Our models are mainly classical and nonrelativistic and typically two-dimensional . The main lines of thought we follow can be traced to Abraham , Alder , Ashurst , Bhattacharya , Boltzmann , Bridgman , Bulgac , Debye , De Rocco , Dettmann , Duvall , Euler , Evans , Fermi , Feynman, Ford , Galton , Gauss , Gibbs , Jaynes , Hamilton , Holian , Kawai , Kratky , Krivtsov , Kusnezov , Lagrange , Landau , Lifshitz , Liouville , Lyapunov , Mareschal , Maxwell , the Mayers , Moran , Morriss , Newton , Nosé , Occam , Pars , Patra , Posch , Rahman , Rice , Ruelle , Sommerfeld , Sprott , Steiner , Stell , Stull , Thoreau , Travis , Uhlenbeck , Vineyard , von Neumann, Wainwright , Wojciechowski . Wood , Zwanzig . Feynman's ideas of pursuing definite examples, along with his and Alder's efforts toward simplicity are always with us .

Most of what you see will be in two dimensions , with graphic illustrations , using FORTRAN and gnuplot and PowerPoint as our main expository tools , not because these are perfect but because we haven't yet found anything better .

In order to teach students rather than course material it is useful to have questions . This is the main job of the student , not just for himself , but for all of us .

Let us thank Baidurya Bhattacharya for making this possible .



Kharagpur Lecture 3

Temperature and Molecular Dynamics

- 1. Ideal Gas Thermometer \rightarrow Temperature/Entropy
- 2. Isokinetic "Gaussian" Molecular Dynamics
- 3. Nosé and Nosé-Hoover Mechanics
- 4. The Boltzmann Equation and Entropy
- 5. The Krook-Boltzmann Equation, η and κ
- 6. Direct Simulation Monte Carlo
- 7. Nosé-Hoover Knots from Yang and Wang

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1. Ideal Gas Thermometer → Temperature/Entropy

| Mechar We ha | nics p ve th | olus Te e luxi | empe ury of | rature using | (and Heat) → Thermodynamics . the ideal-gas temperature scale |
|--|------------------------|-------------------|----------------|-----------------|---|
| Substance and its state | Defining point (range) | | | | |
| | к | °C | °R | °F | |
| riple point of hydrogen | 13.8033 | -259.3467 | 24.8459 | -434.8241 | Titanium melts at T = 3034F . Temperature in the sun = 15,000,000 K . Temperature in the H Bomb is a few times greater than that of the sun . Plotting PV/Nk at low number density defines the ideal-gas temperature scale . |
| riple point of neon | 24.5561 | -248.5939 | 44.2010 | -415.4690 | |
| riple point of oxygen | 54.3584 | -218.7916 | 97.8451 | -361.8249 | |
| riple point of argon | 83.8058 | -189.3442 | 150.8504 | -308.8196 | |
| riple point of mercury | 234.3156 | -38.8344 | 421.7681 | -37.9019 | |
| [riple point of water[note 1] | 273.16 | 0.01 | 491.69 | 32.02 | |
| Melting point ^[note 2] of gallium | 302.9146 | 29.7646 | 545.2463 | 85.5763 | |
| reezing point ^[note 2] of indium | 429.7485 | 156.5985 | 773.5473 | 313.8773 | |
| Freezing point ^[note 2] of tin | 505.078 | 231.928 | 909.140 | 449.470 | |
| Freezing point ^[note 2] of zinc | 692.677 | 419.527 | 1,246.819 | 787.149 | |
| reezing point[note 2] of aluminum | 933.473 | 660.323 | 1,680.251 | 1,220.581 | |
| reezing point[note 2] of silver | 1,234.93 | 961.78 | 2,222.87 | 1,763.20 | |
| reezing point[note 2] of gold | 1,337.33 | 1,064.18 | 2,407.19 | 1,947.52 | |
| Freezing point ^[note 2] of copper | 1.357.77 | 1.084.62 | 2,443,99 | 1.984.32 | |











What about using the **Configurational Temperature** from Landau/Lifshitz ?

$$\langle \nabla^2 \mathcal{H} \rangle = \langle (\nabla \mathcal{H})^2 \rangle / kT \rightarrow kT_C \equiv \langle (\nabla \mathcal{H})^2 \rangle / \langle \nabla^2 \mathcal{H} \rangle.$$

An apparent disadvantage is the occasional vanishing of the denominator . Think about gravitational field forces !

An apparent advantage is the lack of dependence on velocity , where the local velocity might be hard to determine accurately .

Steady rotation increases the forces without increasing temperature so that configurational temperature seems rather unphysical .

2. Isokinetic "Gaussian" Molecular Dynamics

Ordinarily (dK/dt) = – (d Φ /dt). The upshot of a classic concept, Gauss' "Principle of Least Constraint", $\Sigma \delta(F_c)^2 = 0$, is a motion equation of the form (dK/dt) = – (d Φ /dt) + $\Sigma F \cdot v$ as we shall see. Remember that Gauss was famous for "Least Squares" already. This idea is not a panacea, and gives incorrect results sometimes.

Pars' text is a good reference for classical variational principles .



Molecular Dynamics at constant T_{xx} Using a Standard Lagrange Multiplier *

The Lagrange multiplier method leads to

$$\mathcal{H}_{\rm HL} = 2\sqrt{K_q K_p} - K_q + \Phi \ ({\rm Hoover-Leete})$$

where
$$K_q = \left(m\dot{q}^2/2\right)$$
 ; $K_p = \left(p^2/2m\right)$.

This gives the following equations of motion :

{
$$\dot{p} = F$$
 ; $\dot{q} = (p/m)\sqrt{(K_q/K_p)}$ } .

Sample Problem : Three masses with periodic boundary conditions Choose a normal mode with $\omega^2 = 3$ solving three motion equations.

* For references see our arXiv 1303.6190 paper : Hamiltonian Thermostats Fail to Promote Heat Flow





of Particle 1. The x coordinate is $(r/2)\cos(t) = \cos(t) \rightarrow \langle x \ddot{x} \rangle = \langle (d/dt) (x\dot{x}) \rangle - \langle \dot{x}^2 \rangle = 0 - (1/2)$. A good way to start on such problems is to write the Lagrangian (in terms of the coordinates and velocities) in order to discover the momenta and the Hamiltonian equations of motion they obey.





3. Nosé and Nosé-Hoover Mechanics *

* Nosé's 1984 papers [Molecular Physics + Journal of Chemical Physics] and mine in Physical Review A .





Liouville's Steady Flow Equation for Nosé Mechanics

$$(\partial f/\partial t) = -\nabla \cdot (fv) = 0$$
 [Is This Obvious ?].

$$2\mathcal{H} \equiv (p/s)^2 + q^2 + \ln(s^2) + \zeta^2$$
 [Nosé!]

For simplicity, we set the temperature equal to unity in what follows.

$$\mathcal{H} \longrightarrow \dot{q} = (p/s^2) \; ; \; \dot{p} = -q \; ; \; \dot{s} = \zeta \; ; \; \dot{\zeta} = (p^2/s^3) - (1/s)$$

$$\mathcal{H} \longrightarrow f(q, p, s, \zeta) = (1/s)e^{-[(p/s)^2 + q^2 + \zeta^2]/2}$$
.

Because $\nabla \cdot v$ vanishes we just need to show that $v \cdot \nabla f$ vanishes :

$$\begin{split} \dot{q}(\partial f/\partial q) &= (p/s^2)(-qf) \ ; \ \dot{p}(\partial f/\partial p) = (-q)(-pf/s^2) \ ; \\ \dot{s}(\partial f/\partial s) &= (\zeta)[\ (p^2f/s^3) - (f/s) \] \ ; \ \dot{\zeta}(\partial f/\partial \zeta) = [\ (p^2/s^3) - (1/s) \] (-\zeta f) \ . \end{split}$$

* Here f is a conserved quantity , like mass density or probability density , with a velocity v .





















4. The Boltzmann Equation and Entropy

When does Boltzmann's Equation for f(r,p,t) apply ? [1] When the density is low so that PV = NKT. [2] When collisions occur at points (not Enskog, not Knudsen). [3] When collision orientations are random ($P_{xx} = P_{yy}$). These restrictions are all related to the basic assumption $f(r_1, r_2, p_1, p_2) = f(r, p_1)f(r, p_2)^*$ Remarkably, the Boltzmann Equation obeys the Second Law. That is, the Boltzmann Equation is irreversible and provides quantitative viscosities η and conductivities κ . $\dot{f} \equiv (df/dt) = (\partial f/\partial t) + v \cdot (\partial f/\partial r) + (F/m) \cdot (\partial f/\partial v) = (\partial f/\partial t)_{collisions}$ ($\partial f/\partial t$)_{collisions} is calculated from two-body collisions by combining the collisional "losses" with reversed-inverse collisions which give "gains". This expression gives the *comoving* time derivative following the motion.

* These f(. . .) functions are all probability densities in phase spaces .



Boltzmann's Proof of the H-Theorem, $(dS/dt) \ge 0$. $(\dot{S}/Nk) = -(d/dt)\langle f \ln f \rangle = -\int dp_1 \int dp_2 \Gamma_{12} [1 + \ln f] \dot{f} =$ $-\int dp_1 \int dp_2 \Gamma \ln f_1 [f_3f_4 - f_1f_2] = -\frac{1}{4} \int dp_1 \int dp_2 \Gamma \ln(f_1f_2/f_3f_4) [f_3f_4 - f_1f_2]$ For simplicity we imagine that the system is homogeneous and isolated so that integrating over space is unnecessary. Notice also that f is *normalized* so that its integral is constant. The collision rates of corresponding gains and losses are identical as both of them are integrated over the entire velocity space. This *irreversible* result is surprising as the motion is *reversible*. Unless ln f is conserved, as in A + Bv + Cv², the entropy S increases . Evidently equilibrium corresponds to the Maxwell-Boltzmann Gaussian distribution !

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The surprise is usually stated as two paradoxes :

Zermélo : If the equations of motion are reversible then any trajectory obeying the H-Theorem disobeys it if reversed .

Poincaré : If the equations of motion obey Liouville's Theorem then any initial state , no matter how odd , will recur in future .

Boltzmann's Proof of the H-Theorem, $(dS/dt) \ge 0$.

Poincaré : If the equations of motion obey Liouville's Theorem then any initial state , no matter how odd , will recur in future .

To prove this consider a small phase volume $\Delta\Omega$ and follow it long enough that the new volume $\Delta\Omega'$ does not overlap the old . Call $\Delta\Omega''$ all of the volume ever covered (in infinitely long time) which was originally in $\Delta\Omega'$. Then it must be the case that the latter includes $\Delta\Omega$. Otherwise the volume $\Delta\Omega + \Delta\Omega''$ would have to violate Liouville's Theorem . This "Recurrence Theorem" is called Poincaré's Recurrence Paradox . Do not be dismayed that the time required to recur exceeds the age of the Universe for about a dozen argon atoms at liquid density .











6. Direct Simulation Monte Carlo

Direct Simulation Monte Carlo (developed by Græme Bird) provides simple solutions, both analytic and numerical . Divide the space into "zones" or cells, each with several particles . Some cells can act as boundary conditions as in a shock wave . The basic algorithm then advances each particle for a time dt . The number of collisions in each zone is computed from $< |v_{ij}| >$. Pairs of particles in each zone are then selected for collision with The impact parameters are chosen randomly . The advantages of this method are speed and simplicity . The Krook-Boltzmann idea would replace a particle with one drawn from the LTE (Local Thermodynamic Equilibrium) distribution .









Some points of interest that could use investigation Smooth-particle averages provide local quantities : $F(r) \equiv \sum F_j w(r - r_j)$ where $w(r) \propto 1 - 6(r/h)^2 + 8(r/h)^3 - 3(r/h)^4$ Computing the local temperature involves a local Average of two velocity moments : $< (v - < v >)^2 >$. An instantaneous recipe would be handy. One idea is to eliminate the "self contribution" to the local temperature . Irving and Kirkwood, and later Hardy, seem to have confused several researchers .

Percy Williams Bridgman > Quotes > Quotable Quote



"Not only are there meaningless questions, but many of the problems with which the human intellect has tortured itself turn out to be only 'pseudo problems,' because they can be formulated only in terms of questions which are meaningless. Many of the traditional problems of philosophy, of religion, or

of ethics, are of this character. Consider, for example, the problem of the freedom of the will. You maintain that you are free to take either the right- or the left-hand fork in the road. I defy you to set up a single objective criterion by which you can prove after you have made the turn that you might have made the other. The problem has no meaning in the sphere of objective activity; it only relates to my personal subjective feelings while making the decision."

- Percy Williams Bridgman, The Nature of Physical Theory

Ensembles versus trajectories and atomistic mechanics versus continuum mechanics contain examples .























Summary of things it would be good to know up to the present
1. Temperature is best measured with the ideal-gas thermometer .
2. Gauss and Hoover-Leete algorithms are isokinetic and useful .
3. Nosé mechanics is unnecessarily stiff and not very useful .*
4. Nosé-Hoover mechanics is convenient and robust .
5. The Boltzmann Equation covers many applications beyond η , κ .
6. The linear Krook-Boltzmann equation is nearly as useful as is B .
7. Direct Simulation Monte Carlo is a simple tool for gas problems .
8. Knots should appeal to those interested in topology and chaos .

* These problems demonstrate the usefulness of adaptive integration, already explained by Carol .

Things it would be good to think about :

1. How to make a Boltzmann Equation boundary condition for P_{xy}?

2. Can you solve the Krook-Boltzmann equation for a shockwave ?

3. Is entropy a dynamical property of a single dynamical system ?