Lecture 6 non-equilibrium statistical mechanics (part 2)

I will outline two areas in which there has been a lot of work in the past 2-3 decades

1 Derivations of hydrodynamic behaviour

1.1 Independent random walkers

The idea is to show that in a suitable limit the system obeys the equations of (compressible) hydrodynamics; either Euler or Navier-Stokes, depending on what limit is used. (A recent book in this field: "An introduction to the theory of hydrodynamic limits", by József Fritz, Lectures in Math. Sciences, Univ. of Tokyo (2001), ISSN 0919-8180)

Simple example: independent random walkers on an infinite linear lattice with lattice spacing 1. (For rigour, see de Masi & Presutti Math. methods for hydrodynamic limits (Springer 1991) chapter II). At each tick of the clock each walker steps either to left or right, with probability $\frac{1}{2}$ each way.

If the number of walkers at site x at time t is $n(x,t)$, then

$$n(x,t) = \sum_y K(x-y,t)n(y,0) \qquad \boxed{\text{RW}} \tag{1}$$

where

$$\begin{aligned} K(x,t) &= \frac{t!}{[\frac{1}{2}(t+x)]![\frac{1}{2}(t-x)]!}(\tfrac{1}{2})^t \\ &\to (2\pi t)^{-1/2}\exp(-x^2/2t) \qquad \boxed{\text{K}} \end{aligned} \tag{2}$$

as $t \to \infty$ and $x/t \to 0$. The second line is the the DeMoivre-Laplace limit theorem which I took from Feller "Introduction to Probability Theory and its applications" (1961) page 168-170.

To use the limit theorem introduce "macroscopic" scaled variables

$$\xi := \epsilon x, \tau := \epsilon^2 t$$

e.g. if $x = 1$ nanometer, $\xi = 10^{-9}$ metres. On the macroscopic scale, the spacing between lattice sites is ϵ. Then the de Moivre-Laplace theorem in (2) gives

$$\lim_{\epsilon\to 0} K(\xi/\epsilon, \tau/\epsilon^2) = \epsilon(2/\pi\tau)^{1/2}\exp(-\xi^2/2\tau) \qquad \boxed{\text{deML}} \tag{3}$$

We consider an initial probability measure in which initially the number of random walkers at site x is a Poisson distribution with mean $\nu(\epsilon x, 0)$, where with $\nu(\cdot, 0)$ is a given smooth function, independent of ϵ. Choose any ξ_1, ξ_2 with

$\xi_1 < \xi_2$. The expected number of particles at time 0 at lattice sites hvaing ξ values in $[\xi_1, \xi_2]$ is

$$\sum_{x:\xi_1 \le \epsilon x \le \xi_2} \mathbf{E}\, n(x,0) = \sum_{x:\xi_1 \le \epsilon x \le \xi_2} \nu(\epsilon x, 0) \qquad \boxed{\text{line1}} \tag{4}$$

$$\sim \int_{\xi_1}^{\xi_2} \nu(\xi, 0) d(\xi/\epsilon) \qquad \boxed{\text{line2}} \tag{5}$$

where the sign $\sim$ indicates that the ratio of the two sides approaches 1 as $\epsilon \to 0$. The last line of this formula shows the recipe for converting sums over x into integrals over ξ. At time $t := \tau/\epsilon^2$, the expected number of particles having ξ values in $[\xi_1, \xi_2]$ is

$$\begin{aligned}
\sum_{x:\xi_1 \le \epsilon x \le \xi_2} \mathbf{E}\, n(x,t) &= \sum_{x:\xi_1 \le \epsilon x \le \xi_2} \sum_y K(x-y,t) \mathbf{E}\, n(y,0) \quad \text{by (1)} \\
&= \sum_{x:\xi_1 \le \epsilon x \le \xi_2} \sum_y K(x-y,t) \nu(\epsilon y, 0) \quad \text{by (4)} \\
&\sim \int_{\xi_1}^{\xi_2} d(\xi/\epsilon) \int_{-\infty}^{\infty} d(\eta/\epsilon) K((\xi-\eta)/\epsilon, t) \nu(\eta, 0) \quad \text{by (5)} \\
&\sim \epsilon^{-1} \int_{\xi_1}^{\xi_2} d\xi \int_{-\infty}^{\infty} d\eta \frac{\exp(-(\xi-\eta)^2/2\tau)}{(2\pi\tau)^{1/2}} \nu(\eta, 0) \quad \text{by (3)} \\
&= \int_{\xi_1}^{\xi_2} \nu(\xi, \tau)\, d(\xi/\epsilon) \qquad \boxed{\text{calcn}} \qquad (6)
\end{aligned}$$

where

$$\nu(\xi, \tau) := \int_{-\infty}^{\infty} d\eta \frac{\exp(-(\xi-\eta)^2/2\tau)}{(2\pi\tau)^{1/2}} \nu(\eta, 0) \qquad \boxed{\text{intfor}} \tag{7}$$

The expected number of particles with ξ values in the interval $[\xi_1, \xi_2]$ at time t is thus given by a formula analogous to (5),

$$\sum_{x:\xi_1 \le \epsilon x \le \xi_2} \mathbf{E}\, n(x, \epsilon^2 \tau) \sim \int_{\xi_1}^{\xi_2} \nu(\xi, \tau)\, d(\xi/\epsilon) \tag{8}$$

Moreover, by the law of large numbers, the actual number of particles in this interval will fluctuate away from this mean by a relative amount which vanishes in the limit $\epsilon \to 0$. So in this limit, the hydrodynamic behaviour is described exactly by the function $\nu(\xi, \tau)$, which is given in terms of its initial value by the integral formula (7).

Differentiating with respect to t and using the properties of the heat kernel, we find that ν satisfies the diffusion equation

$$\partial \nu(\xi, \tau)/\partial \tau = \tfrac{1}{2} \partial^2 \nu / \partial \xi^2 \tag{9}$$

1.2 Other results for stochastic dynamics

There are several other results of this kind (the following information comes from Lebowitz, Presutti and Spohn J Stat Phys **51** (1988) 841-862).

1. Independent particles with asymmetric random jumps, i.e. the probability of a jump to the right is p and to the left is $q := 1 - p$. In this case things happen faster, and a different scaling is used, $\bar{\tau} := \epsilon t$ not $\tau = \epsilon^2 t$. The macroscopic equation is now of first order

$$\partial\nu/\partial\bar{\tau} + (p-q)\partial\nu/\partial\xi = 0 \tag{10}$$

2. Same as previous but with on-site exclusion (i.e. no more than one particle per site, and a jump to an occupied site is forbidden, so that $n \leq 1$.) This model is called the asymmetric exclusion process. The macroscopic eqn is now Burgers' eqn

$$\partial\nu/\partial\bar{\tau} + (p-q)\partial[\nu(1-\bar{\nu})]/\partial\xi = 0 \tag{11}$$

   An important feature is that this equation can develop shocks. There has been much recent work on the ASE process. An important contribution is Derrida's exact solution described in Derrida, Evans, Hakim and Pasquier J Phys. A **26** 1493-1517 (1993). This has been applied to the problem of shocks by Derrida et al J Stat Phys **73** 813-842 (1993)

3. Same as previous but now we go back to the longer time scale, $\tau = \epsilon^2 t$ and make $p - q = \alpha\epsilon$ for some constant α . The on-site exclusion is retained. The macroscopic eqn is now

$$\partial\nu/\partial\tau + \alpha\partial[\nu(1-\nu)]/\partial\xi = \tfrac{1}{2}\partial^2\nu/\partial\xi^2 \tag{12}$$

   (Fritz J Stat Phys **47** 551-572 (1987), Guo, Papanicolaou and Varadhan Comm Math Phys **118** 31-59 (1988): "one of the most beautiful results in the field" — Lebowitz et al.(1988)).

By introducing suitable off-site interactions into the model one can produce derivations of other hydrodynamic-type equations, e.g. Allen-Cahn eqn, also known as Ginzburg-Landau (see chapter VIII of de Masi and Presutti's book).

1.3 Hamiltonian dynamics

For systems of particles with Hamiltonian dynamics, it is more difficult to get rigorous results. There is a proof of the analogue of Euler's equation for a one-dimensional system of hard rods by Boldrighini, Dobrushin and Suhov 1983, Dobrushin 1989 using the "convective" scaling of items 1,2 above. The hydrodynamic equation obtained is (for rods of unit length)

$$\frac{\partial}{\partial\tau}f(\xi,v,\bar{\tau}) + \frac{\partial}{\partial\xi}\left(v + \frac{1}{1-\nu}\int dw(v-w)f(\xi,w,\bar{\tau})\right)f(\xi,v,\bar{\tau}) = 0 \tag{13}$$

BDS

where $f(\xi, v, \bar{\tau})\, d\xi\, dv$ is the single-particle distribution function, i.e. the number of particles having scaled postions ξ and velocities v in the interval $[\xi, \xi + d\xi] \times [v, v + dv]$. It is related to ν by $\nu(\xi, \bar{\tau}) = \int f(\xi, v, \bar{\tau})\, dv$. For more information see section 3.3 of Spohn's book "Large Scale Dynamics of Interacting particles" (Springer 1991).

2 Non-Hamiltonian dynamics

2.1 The Gaussian thermostat

Suppose you want to use molecular dynamics to calculate, say, the viscosity of a liquid at a large value of the shear — perhaps in order to see whether it is non-Newtonian. This can be done by altering the equations of motion (or the boundary conditions) so that the steady state has a shear. There are various ways to do this, but they all involve the Lees-Edwards boundary condition (1972, see Evans & Morriss "Statistical Mechanics of Non-equilibrium Liquids" (1990), page 133) To simulate a shear rate gamma in a 2-D liquid in a periodic box of side L, the BCs at $x = \pm L$ are as usual, i.e. if a particle reaches the point $(0, y)$ with velocity $(u, v)(u < 0)$ it is replaced at the point (L, y) with the same velocity, and contrariwise. But if it reaches the point $(x, 0)$ with velocity $(u, v)(v < 0)$ it is replaced at the point $(x + \gamma L t, L)$ with velocity $(u + \gamma L)$, and there is a similar rule for particles that reach a point (L, y). This imposes a rate of shear, and the shear stress is a dynamical variable whose value can be found from the dynamical state of the system, and averaged over many runs, or over time.

The dificulty is that the modified system does not conserve energy: its energy, and therefore temperature, changes as the simulation proceeds. To keep the temperature from changing and experimentalist would use a thermostat, and the simulation people now do the same thing. Rather than try to model the complex interaction with a real thermostat, the usual method is the 'Gaussian thermostat' (Hoover, Ladd and Moran Phys Rev Lett **48** 1818 (1982); see pp. 36-42 of Evans & Morriss' book). The idea is to modify the eqns of motion using Gauss' 'principle of least constraint'. A simple way of using it is to require that the total kinetic energy of the system must remain constant. The application of Gauss's principle then leads to the modified version of Newton's second law

$$m_i d^2\mathbf{r}_i/dt^2 = \mathbf{F}_i - \lambda m_i d\mathbf{r}_i/dt \qquad \boxed{\text{friction}} \tag{14}$$

where

$$\lambda = \frac{\sum \mathbf{F}_i \cdot \dot{\mathbf{r}}}{\sum m_i \dot{\mathbf{r}}^2} \tag{15}$$

Most of the time λ is positive, and then the new term looks like a frictional force. It turns out that these models lead to some interesting mathematics, which is a topic of current interest in the field.

An illustration is the model of electrical conductivity consisting of a gas of N electrically charged particles with two-body interactions moving on a billiard

table with circular scatterers. In this case the force F is the sum of the interparticle forces, the forces due to the scatterers and the constant electric force, and the eqns of motion are as given above. (The theory of this model in the case $N = 1$ is studied by Chernov, Eyink, Lebowitz and Sinai, Comm. Math. Phys **154** 569-601 (1993). I have not seen this paper. A numerical study ($N > 1$) was done by Bonetto et al (Physica D **105** 226-252 (1997))).

2.2 SRB measures

In addition to the results about specific models and simulation schemes using non-Hamiltonian dynamical laws such as 14, people are beginning to develop theory generalizing the traditional theory (which I outlined in lectures I and II) to non-Hamiltonian systems. Here are some of the main points that have come out so far:

- Instead of conservation of phase space volume there is now a contraction, since the eqns of motion now look like

$$\begin{aligned} dp/dt &= -\partial H/\partial q - \lambda p \\ dq/dt &= \partial H/\partial p \end{aligned} \tag{16}$$

  leading to

$$\partial \dot{p}/\partial p + \partial \dot{q}/\partial q = -\lambda,$$

  and λ is positive on average (a frictional force). The logarithm of the rate of contraction is called the entropy production.

- Instead of weak convergence to a microcanonical ensemble, the individual orbits are expected to approach an attractor in phase space

- The measure is expected to converge to a measure on the attractor called the SRB measure. The SRB measure is defined as the long-time weak limit of the time average of any measure which initially is absolutely continuous with respect to the Riemannian volume element on phase space and is zero outside the basin of attraction of the attractor. The formula is

$$\text{weak} \lim_{t\to\infty} t^{-1} \int_0^t ds (f^s) * m$$

  where m is the inital measure and f is the evolution operator. (Eqn 10 on page 408 of Ruelle's authoritative review "Smooth dynamics and nonequilibrium statistical mechanics" J Stat Phys **95** 393-468 (1999))

- Corresponding to the hypotheses about ergodicity and mixing in equilibrium stat. mech we have Ruelle's "chaos hypothesis" according to which the attractor is an "Axiom A" attractor; this means that it has a certain type of hyperbolicity.

- The fluctuation theorem of Gallavotti and Cohen (Phys Rev Letters **74** 2694-2697 (1995), J Stat Phys **80** 931-970; see also Evans et al Phys Rev Lett **71** 2401 (1993)), which is a consequence of Ruelle's chaos hypothesis. The theorem relates the SRB probability of a given trajectory with that of its time inverse. For a canonical measure these probabilities would be equal (by microscopic reversibility). For the SRB measure the ratio of the two probabilities is equal to the Jacobian relating phase-space volumes at the initial and final points on the trajectory. This theorem has been tested experimentially, both in computer simulations (see paper by Bonetto et al cited below) and in the laboratory (Wang et al Phys Rev Letters **89** 050601-1 (2002).