DERIVATION OF NONLINEAR ONSAGER RELATIONS FROM STATISTICAL MECHANICS

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Abstract

The long road that starts from the microscopic equations of motion and ends with the phenomenological equations of the experimenter, is sketched. One type of system leads to nonlinear macroscopic equations, but no reciprocal relations are found. The other type (called diffusive type) leads to a nonlinear Fokker–Planck equation. For low temperature the fluctuations are small and one is left with a set of nonlinear deterministic equations. They obey the Onsager–Casimir relations.

Keywords: statistical mechanics; nonlinear Onsager relations.

The way in which Onsager arrived at his celebrated reciprocal relations was a stroke of genius. He managed to combine on the one hand equilibrium statistical mechanics with, on the other hand, bits of information about fluctuations and then to deduce relations among the phenomenological co-efficients in the macroscopic laws governing the irreversible behaviour. It has proved hard to extend this feat to nonlinear macroscopic laws (although Peter Mazur showed that Onsager was close [1]). Some attempts are re-viewed by Verhás [2]. Unfortunately I am not a genius and must therefore plod along in a systematic way from the very first principles of statistical mechanics to arrive in a reliable manner at reciprocal relations. It is a long way, which in the present context I can only sketch. A large number of details have to be omitted, for which I refer to [3].

The starting point in the classical case is formed by the Hamiltonian equations of motion for N particles in a volume Ω with reflecting walls,

$$\dot{q}_k = \frac{\partial H}{\partial p_k}, \qquad \dot{p}_k = -\frac{\partial H}{\partial q_k}. \tag{1}$$

An ensemble of such systems is described by a density $\rho(q, p, t)$ in $6N$ dimensional phase space, whose evolution can be written using Poisson brackets:

$$\dot{\rho}(q, p, t) = \{H, \rho\}. \tag{2}$$

A stationary ensemble with energy E is

$$\rho^\epsilon(q, p) = \delta[H(q, p) - E]. \tag{3}$$

Note that the Liouville equation (2) is logically equivalent to (1): if one knows the solutions of (1) one knows those of (2) and vice versa. Introducing an ensemble is *not* an aid to solving the equations of motion but merely a preparation for an approximate treatment.

Coarse-graining is an indispensable step in statistical mechanics. Suppose one has a set of observable quantities, given as functions $A_r(q, p)$ in phase space. Define *phase cells* as subregions of phase space delineated by

$$a_r < A_r(q, p) < a_r + \Delta a_r \qquad (\text{all} \quad r). \tag{4}$$

The margins Δa_r are determined by the accuracy of the observations. The coarse-grained distribution $P(a_1, a_2, \dots)$ in the observational a-space is given by

$$P(a_1, a_2, \dots) = \int_{a_r < A_r(q,p) < a_r + \Delta a_r} \rho \, dq \, dp. \tag{5}$$

This is a projection: from ρ follows uniquely P, but not vice versa. Stationary ρ^e give stationary P^e.

The coarse-grained P, in contrast to ρ does not satisfy an autonomous evolution equation of differential type (does not constitute a semi-group). The reason is that one has lost the information about the details of the distribution ρ inside each phase cell. As a remedy one makes the following randomness assumption: The detailed distribution does not matter, all that matters for the disevolution of P is the total occupation in the cells, i.e. (5). Then there exists a probability that a system in cell a_r has moved after a small time Δt into a cell at a'_r, which we denote by $\Delta t \, W(a'|a) \, \Delta a'$. This leads to the *master equation*

$$\dot{P}(a; t) = -\int W(a'|a) \, da' \cdot P(a; t) + \int W(a|a') P(a'; t) \, da'. \tag{6}$$

Note that after each Δt we have to make the same assumption again. This *repeated randomness assumption* is a generalization of Boltzmann's 'Stosszahlansatz'. It is a part of *all* derivations of master equations, however cleverly concealed. It is very drastic inasmuch as it breaks the time symmetry by stipulating that one must randomize at the start of each Δt.

The justification of this assumption is still a mystery. One thing is clear, the proper choice of the macrovariables A_r is crucial, and is not determined by the taste of the experimenter. For instance, they must somehow incorporate all correlations that live longer than Δt. And they must vary so slowly that they are practically continuous, i.e. they do not vary much during Δt. These are the reasons why one cannot add ad libitum new variables, as is done in extended thermodynamics.

In *quantum statistical mechanics* the starting point is the Schrödinger equation for the N particles

$$i\hbar \dot{\Psi}(q_1, q_2, \ldots, p_1, p_2, \ldots) = H\Psi. \tag{7}$$

The macrovariables are those hermitian operators A_r in Hilbert space that are slowly varying; that means that in the representation in which H is diagonal their matrix elements are concentrated in a narrow band along the diagonal, narrow compared to the experimental margin ΔA_r.

It is essential in quantum statistical mechanics to realize that the level density is homogeneous. Phase cells are linear subspaces of the total Hilbert space and still have a huge number of dimensions. They are constructed in such a way that in each of them the variables A_r have a value a_r, well defined within the experimental error ΔA_r. Hence they commute with each other. The occupation P of the phase cell is given by the square of the component of Ψ in that cell. In this way one obtains again (6), [4].

The reason why quantum mechanics does not affect the formulation of the master equation is visualized by the following picture. Quantum mechanics breaks up the phase space into grains of order $\hbar$. They are much finer than the coarse grains ΔA_r determined by the macroscopic observations. This explains how the description on the macroscopic level has become classical, in terms of probabilities P instead of probability amplitudes Ψ. Of course, the construction of the A_r and the values of the transition probabilities W do reflect the underlying quantum mechanics.

Consider the *time reversal transformation*, which in classical language reads

$$t \longrightarrow -t, \qquad q \longrightarrow q, \qquad p \longrightarrow -p. \tag{8}$$

Suppose $A_r(q, -p) = \varepsilon_r A_r(q, p)$ where $\varepsilon_r = \pm 1$ for even and odd variables. H must be even so that P^ϵ is invariant. Once the master equation (6) has been accepted it can be proved rigorously that W obeys *detailed balance*:

$$W(a|a')P^\epsilon(a') = W(\varepsilon a'|\varepsilon a)P^\epsilon(a). \tag{9}$$

(I do not consider Hamiltonians that are not invariant for (8), as in the presence of a magnetic field or an overall rotation [5]) In quantum mechanics the language is different but the result (9) is the same.

Having established the master equation for the occupation probabilities of the phase cells we now have to extract macroscopic deterministic equations from it, such as hydrodynamics, Ohm's, law, rate equations of chemical reactions, etc. This is achieved by the *system size expansion*, applicable whenever W involves a large parameter, e.g. the volume Ω, capacity C, particle number N. Write the variables a_r as the sum of a macroscopic part and a fluctuating part

$$a_r = \Omega\varphi_r(t) + \Omega^{1/2}\xi_r, \qquad P(a, t) = \Pi(\xi, t). \tag{10}$$

Consider this as a transformation from the a_r to the new variables ξ_r, the functions φ_r to be fixed presently. Define mean and variance of the jumps:

$$m_r(a) \quad = \int (a_r' - a_r) W(a'|a)\, da' = m_r^{(0)}(a) + \Omega^{-1} m_r^{(i)}(a) + \cdots, \quad (11)$$

$$\sigma_{rs}(a) \qquad = \int (a_r' - a_r)(a_s' - a_s) W(a'|a)\, da' = \sigma_{rs}^{(0)}(a) + \cdots. \quad (12)$$

Substitute all this into the master equation to get an equation for the probability $\Pi(\xi, t)$ and collect powers of Ω. There are some ominous terms of order $\Omega^{+1/2}$, but they can be made to cancel by requiring $\varphi_r(t)$ to obey

$$\dot{\varphi}_r(t) = m_r^{(0)}(\varphi). \quad (13)$$

This is the macroscopic deterministic phenomenological equation. It is nonlinear and there is no Onsager relation.

The terms of order Ω^0 yield

$$\frac{\partial \Pi(\xi, t)}{\partial t} = -m_{r;s}^{(0)}(\varphi) \frac{\partial}{\partial \xi_r} \xi_s \Pi + \frac{1}{2} \sigma_{rs}^{(0)}(\varphi) \frac{\partial^2 \Pi}{\partial \xi_r \partial \xi_s}. \quad (14)$$

(Summation implied: $m_{r;s}^{(0)}$ is the derivative of $m_r^{(0)}$ with respect to a_s.) This is a linear Fokker–Planck equation with time-dependent coefficients. It describes the fluctuations about the macroscopic value in Gaussian approximation.

In our Ω-expansion we tacitly assumed that $m_r^{(0)} \neq 0$ and that the solutions $\varphi_r(t)$ of (13) tend to an equilibrium point φ_r^e. In other systems it may happen that $m_r^{(0)}$ vanishes identically: I call this the *diffusion type*. The expansion of the master equation then takes a different form: its lowest order in Ω^{-1} turns out to be (after some rescaling)

$$\frac{\partial P(a, t)}{\partial t} = -\frac{\partial}{\partial a_r} m_r^{(1)}(a) P + \frac{1}{2} \frac{\partial^2}{\partial a_r \partial a_s} \sigma_{rs}^{(0)}(a) P. \quad (15)$$

This is a *nonlinear* Fokker–Planck or diffusion equation. By some trivial rearranging of terms

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial a_r} K_r(a) P + \frac{1}{2} \frac{\partial}{\partial a_r} \left(\sigma_{rs}^{(0)}(a) P^e \frac{\partial}{\partial a_s} \frac{P}{P^e} \right) \quad (16)$$

$$K_r(a) = m_r^{(1)}(a) - \frac{1}{2P^e} \frac{\partial}{\partial a_s} \sigma_{rs}^{(0)}(a) P^e. \quad (17)$$

The first term in (16) has the form of a Liouville equation belonging to the deterministic equation of motion

$$\dot{a}_r = K_r(a). \quad (18)$$

The second term is dissipative, as is demonstrated by the following H-theorem

$$\frac{d}{dt} \int \frac{P^2}{P^\epsilon} \, da = - \int P^\epsilon \left(\frac{\partial}{\partial a_r} \frac{P}{P^\epsilon} \right) \sigma_{rs}^{(0)} \left(\frac{\partial}{\partial a_s} \frac{P}{P^\epsilon} \right) \, da \leq 0. \tag{19}$$

Application of detailed balancing (9) to the differential operator in (16) is a bit tricky but can be done, with the result

$$\varepsilon_r K_r(\varepsilon a) = -K_r(a), \qquad \varepsilon_r \varepsilon_s \sigma_{rs}^{(0)}(\varepsilon a) = \sigma_{rs}^{(0)}(a). \tag{20}$$

This shows that (18) is invariant for time reversal. Hence the two terms in (16) represent the reversible and the irreversible evolution, respectively.

To extract from (15) or (16) a deterministic phenomenological equation one has to choose once again an expansion parameter. The temperature T is an obvious choice since for low T the fluctuations are small. Accordingly we assume that $\sigma_{rs}^{(0)}$ scales with T:

$$\sigma_{rs}^{(0)}(a, T) = T\tilde{\sigma}_{rs}(a). \tag{21}$$

For any particular system this can be checked using the definition (12). One also knows how P^ϵ varies with T:

$$P^\epsilon(a) = C \exp[-F(a)/T]. \tag{22}$$

Substitute (21) and (22) into (16) and collect powers of T

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial a_r} \left[K_r - \frac{1}{2}\tilde{\sigma}_{rs} \frac{\partial F}{\partial a_s} \right] p + \frac{T}{2} \frac{\partial}{\partial a_s} \tilde{\sigma}_{rs} \frac{\partial P}{\partial a_s}. \tag{23}$$

Now take the limit $T \longrightarrow 0$ so that the fluctuation part vanishes and one is left with a Liouville equation belonging to a deterministic equation for a_r, namely

$$\dot{a}_r = K_r(a) - \frac{1}{2}\tilde{\sigma}_{rs}(a)\frac{\partial F(a)}{\partial a_s}. \tag{24}$$

The first term is reversible and therefore mechanical, the second term is damping.

The second term in (24) has the familiar form of the rate equations (or regression equations). The thermodynamic forces are

$$X_s = -\frac{\partial F}{\partial a_s}. \tag{25}$$

They need not be linear in the a_r, as mentioned by MAZUR [1]. Since F is invariant under time reversal (8), the force X_s has the same parity as a_s.

The familiar rate coefficients are

$$L_{rs} = \frac{1}{2}\tilde{\sigma}_{rs}(a) \tag{26}$$

and need not be constants. According to (20) they obey the Onsager reciprocity relations, including Casimir's extension.

As we used T as an expansion parameter our treatment formally applies to isothermal cases only. This can be remedied by choosing as expansion parameter some averaged or representative temperature and including the deviation of the actual temperature as one of the a_r.

1. Summary

From the microscopic equations we obtained the master equation (6) at the expense of the repeated randomness assumption. The matrix W of transition probabilities obeys (9). When it involves a size parameter Ω one may expand in powers of $\Omega^{-1/2}$. Either this gives a macroscopic equation (13) with Gaussian fluctuations (14), or it gives a diffusion equation (15). In the latter case a set of deterministic equations (24) may be extracted by expanding in T. These equations are nonlinear and yet subject to the reciprocal relations of Onsager–Casimir.

References

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