

Strange systems in statistical mechanics

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Abstract. A number of rather unexpected behaviours in various systems are reviewed. Namely, it is shown that a macroscopic system having chaotic dynamics may nevertheless display undamped harmonic radial oscillations. Next, we show that small systems in an external field may have spatially dependent kinetic temperatures in equilibrium. Further, we can also show that the kinetic temperatures of different particle species in the same region of space will in general not assume the same values. Finally, we discuss the remarkable way in which the zero'th law of thermodynamics can sometimes appear to be violated in systems having long-range interactions.

1 Introduction

Since Alberto Robledo has often shown us unusual behaviour in statistical mechanics, whether related to the edge of chaos, or anomalous statistics, it is surely fitting to honour him by a discussion of anomalies in various systems which have come to our notice. To do this, we shall consider situations neither far from equilibrium nor involving dissipation. Rather, we shall look at ordinary Hamiltonian system, at equilibrium or close to it, and see whether we find a worthy birthday present for Alberto.

We shall look at three different systems. The first will simply be an arbitrary N -particle system, in arbitrary dimension, including the “physical” three-dimensional case. The only restriction on the system is that the interparticle interactions be homogeneous of degree -2 . We shall additionally assume that, instead of being confined by a box, as is usual in statistical mechanics, this system is confined by a harmonic potential. In that case [1–3], we shall see that the system displays undamped, harmonic radial oscillations. In other words, the radius of gyration of the system oscillates in a purely harmonic manner. Thus this oscillation displays no noise. This is not the result of some approximation, but an exact consequence of the Hamiltonian equations of motion.

Why should this qualify as “strange”? As follows from the results presented in [2,3], the oscillation is found to be adiabatic, defining entropy appropriately. Under

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these circumstances it can be shown that the temperature oscillates together with the radius of gyration. Hence, if the amplitude of the radial oscillations does not diminish, neither does that of the temperature oscillation. The system thus does not approach thermodynamic equilibrium.

We might look for several “excuses” for such behaviour: perhaps the system is not sufficiently chaotic? That is not generally the case. In three dimensions, it has been shown numerically that the system is quite chaotic, having clearly positive Lyapunov exponents. It is true that there exists a case in which the system is fully integrable: if the system is one-dimensional and all the interactions between the particles are identical (something we did not assume above) then the system does have the following amazing feature, as shown by Calogero [4]: it is *isochronous*, in other words, starting from any given *microscopic* configuration, after a given period, which is the same as that of the confining harmonic oscillator potential, the same microscopic configuration is recovered, that is, the orbit is *periodic*. In this case, therefore, it is not merely the collective variable describing the radius of gyration of the system which oscillates over a short period: it is the entire microscopic configuration which thus recurs periodically.

But in the general case we are discussing, this is most definitely not the case. So what is happening? In fact, as we shall show, the system in question displays an unusual symmetry, related to a kind of conformal invariance, which allows the radius of gyration, as well as some other collective variables, to decouple completely from the microscopic variables. So, whereas the latter may, and in fact generally do, display irreversible behaviour, this remains unconnected to the behaviour of the radius of gyration and a few other related collective variables. But, whereas the microscopic variables are without influence on the collective ones, the reverse is not true: such quantities as the temperature depend, via a scaling law, on the radius of gyration.

The consequences of such behaviour, for example, on thermodynamics, are up to now still rather unclear. In any case, it appears to be some kind of counterexample to the claim often made that a macroscopic system, started in any initial condition, will eventually reach thermal equilibrium. This claim was made, for example, by Hänggi and baptised as the -1 'st law of thermodynamics [5].

Let us now consider an altogether different system: we assume that we have a comparatively small system (we may think, say, of a system with $N \sim 100$). The peculiar effects which we shall be examining will be of order $1/N$, so they will be of no real interest for truly macroscopic systems.

Consider such a system at fixed energy, hence in the *microcanonical* ensemble. Let us further assume the system to be subjected to an external field \mathcal{E} acting on the various kinds of particles present in the system according to their respective charges. We then [6] claim that the *kinetic temperature* of these particles show unexpected features: first, it displays a *spatial gradient* in thermal equilibrium. Under the normal definition of temperature, this clearly should not be the case, since temperature is, by definition, an equilibrium parameter. In other words, the very nature of equilibrium is synonymous with the constancy of temperature. It will, most correctly, be objected that the kinetic temperature is not the thermodynamic temperature in the microcanonical ensemble.¹ This is, of course, correct. Yet this leads to another question: how could we, in any way, say that there is no spatial gradient for thermodynamic temperature? Whereas it is straightforward to define local kinetic temperature, it is not obvious how to do the same for the microcanonical thermodynamic temperature.

An additional remarkable fact in this context is the following: not only is the kinetic temperature spatially dependent, it also does not reach the same value between

¹ In the canonical ensemble, it follows from the equipartition theorem that kinetic temperature and thermodynamic temperature coincide. This remains true independently of system size.

different species having different charges, even at the same height. Thus, if we look at the average kinetic energy of a highly charged particle at sufficient height, we find that this will markedly differ from the average kinetic energy for a neutral, or less charged particle, at the same height. This arises even though the two particle species interact.

This clearly goes very much against the usual views: we ordinarily think – ever since Boltzmann [7] gave us the insights embodied in his equation – that interactions between particles of whatever nature will always eventually result in equilibration of the various species' kinetic energies, yielding thereby the unique concept of temperature. That these arguments might actually fail in the presence of an external field, such as the one provided by gravity, was argued in a highly interesting paper by Loschmidt [9]. Unfortunately, his arguments were not fully cogent², but the small system results we obtain may, perhaps, be viewed as a small-scale realisation of his claims.

Finally, to round off this tour of marvels (or, depending on your attitude, repellent anomalies) in statistical mechanics, we review a well-known set of results involving systems having long-range interactions and the zero'th law of thermodynamics. In particular, an example is been given, in which, if a weak thermal contact is established between two identical systems – same energy per particle, same Hamiltonian with the same coupling constants – the composite system shows a non-trivial time evolution. Since identical systems should, under any possible view, have the same temperature, this tells us that a weak thermal contact between two systems having the same temperature can nevertheless lead to changes in the values of the macroscopic variables characteristic of the system.

Finally, we may ask what the point of the whole exercise is. Surely, it cannot be to state that the laws of thermodynamics are wrong, or worthless. Indeed, if one looks carefully at all these instances, none contradict flatly thermodynamics. We did try, we admit, to get a perpetual motion machine of the second kind out of some of these systems. As none of you will be surprised to hear, we failed in all cases. So, at the very least, the Second Law remains untouched, recalling Eddington's remarks [8]: "If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations, then so much the worse for Maxwell's equations. If it is found to be contradicted by observation, well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation".

Nevertheless, we believe some deeper understanding can be gleaned from concrete examples in which we see the laws of thermodynamics play out, at least, in a way we might not have expected. It broadens, perhaps, our horizons, and may make us less prone to shout our opponents down with the argument that their claims "go against the laws of thermodynamics".

2 Undamped oscillations

We discuss now the system with undamped oscillations. The system under consideration is characterised by the Hamiltonian

$$H(\vec{r}; \vec{p}) = \frac{1}{2} \sum_{n=1}^N (p_n^2 + \Omega^2 r_n^2) + V^{(-2)}(\vec{r}), \quad (1a)$$

$$\Omega \equiv \Omega(N) = \omega N^{-1/d}. \quad (1b)$$

² in other words, wrong.

Here the notation is as follows: the positive integer N denotes the number of particles; the “coordinates” d -vector $\vec{r}_n \equiv (x_{n1}, \dots, x_{nd})$ identifies the position in d -dimensional space (with d a positive integer) of the n -th particle and depends on the time variable t , $\vec{r}_n \equiv \vec{r}_n(t)$ (but often this time dependence is suppressed); the notation \vec{r} denotes the $N \times d$ -matrix with elements x_{nj} where $n = 1, \dots, N$ and $j = 1, \dots, d$; likewise for the “momentum” N -vector $\vec{p}_n \equiv (p_{n1}, \dots, p_{nd}) \equiv \vec{p}_n(t)$ and the $\vec{p}(t)$; of course $p_n^2 = \vec{p}_n \cdot \vec{p}_n \equiv \sum_{j=1}^d p_{nj}^2$ and $r_n^2 = \vec{r}_n \cdot \vec{r}_n \equiv \sum_{j=1}^d x_{nj}^2$; superimposed dots indicate time-differentiations; ω is a positive constant (independent of N), while the N -dependence of Ω (see (1b)) is introduced to scale the size of the container so that it entails an equilibrium configuration of the system the volume of which is proportional to the number N of particles, as appropriate in order to eventually discuss the thermodynamic limit $N \rightarrow \infty$; and we trust the rest of the notation to be self-evident.

The crucial limitation consists in considering only potentials $V^{(-2)}(\vec{r})$ such that

$$V^{(-2)}(\lambda \vec{r}) = \lambda^{-2} V^{(-2)}(\vec{r}) \quad (2)$$

for all λ .

We now argue that such a system has undamped radial oscillations. To this end, we introduce the following three quantities:

$$Q = \sum_{n=1}^N r_n^2 = \sum_{n=1}^N \sum_{j=1}^d x_{nj}^2, \quad (3a)$$

$$D \equiv D(\vec{r}, \vec{p}) = \sum_{n=1}^N \vec{r}_n \cdot \vec{p}_n. \quad (3b)$$

$$H_0 = \frac{1}{2} \sum_{n=1}^N p_n^2 + V^{(-2)}(\vec{r}). \quad (3c)$$

It is straightforward to verify that the Poisson brackets of Q , H_0 and D , defined via $\{p_i, q_j\} = \delta_{ij}$, close to a Lie algebra, as follows:

$$\{H_0, D\} = 2H_0, \quad \{H_0, Q\} = 2D, \quad \{Q, D\} = -2Q. \quad (4)$$

From this follows immediately that, if the dynamics is defined by the Hamiltonian (1), which is given by a linear combination of H_0 and Q , the three quantities defined in (3) satisfy a closed set of equations, which are easily solved; the quantity Q then displays harmonic oscillations. If the center of mass is at the origin, then Q is equal to the radius of gyration, so that its oscillations correspond to radial compressional oscillations.

Let us discuss the meaning of these results: it follows from the commutation relations between Q , H_0 and D , that the following quantity is conserved:

$$\Xi = QH_0 - \frac{D^2}{2}. \quad (5)$$

If we therefore wish to do statistical mechanics for such a system, we should limit ourselves to constant values of Ξ , in the same manner as is done in systems having rotational invariance, for which we must specify the value of angular momentum.

But there is a problem with defining the “thermodynamic equilibrium state” as the “energy surface” Σ defined by the energy E and the extra conservation law Ξ . Indeed, to each point of Σ , there is a macroscopic orbit describing the variation of Q , H_0 and D due to the dynamics of H . This orbit remains inside Σ , so that Σ contains

elements which have macroscopically different values for such macroscopic observables as D , H_0 and Q . This means that this “equilibrium state” cannot be viewed as the description of a specific system, since macroscopic observables are not sharply peaked. The way to escape this problem would be, of course, to specify, additionally to Ξ , the values of Q and H_0 , for example. Doing this, however, leads to nonstationary states. Thus, the system, as presented, does not approach thermodynamic equilibrium.

3 The kinetic temperature of small systems in an external field

Let us now discuss the problem of a small system of N particles, in an external field \mathcal{E} . The Hamiltonian is

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + V(\vec{x}_1, \dots, \vec{x}_N) + q\mathcal{E} \sum_{i=1}^N x_{i,1} \quad (6)$$

with notation similar to that introduced in Section 2. The field is in the x direction and the system is unbounded in the direction of positive x , whereas it is confined by a hard wall at $x = 0$.

Let us first make an obvious remark on this system in the canonical ensemble: due to the equipartition theorem, the kinetic temperature, that is, the time average of the kinetic energy of any given particle, is equal to the thermodynamic temperature, which itself is necessarily constant throughout any system at equilibrium. As a consequence, it follows that the kinetic energy of a particle conditioned on the particle being at a given height x is independent of x .

Let us now consider this system in the *microcanonical ensemble*. There, the equipartition theorem does not hold. Rather we have [12]

$$k_B T_M = \frac{2}{dN} \langle K^{-1} \rangle^{-1} \quad (7)$$

where K stands for the total kinetic energy of the system, d is the dimensionality of ambient space, and N is the number of particles. Here we assume that the microcanonical entropy is defined as the logarithm of the volume enclosed by the energy surface. Other definitions are, of course, possible, leading to minor changes in this formula.

Of course, whereas it is straightforward to define a *local* form of the kinetic temperature, it seems impossible to do the same for the microcanonical temperature (7).

It thus becomes a legitimate question to ask whether the kinetic energy, with its ordinary definition, is in fact independent of the height x . Both numerically and analytically [6] one finds indeed that kinetic temperature generically decreases with height, with a gradient of the order of $1/N$. The intuitive justification of this effect, already found in [9], is straightforward: for a single particle to reach a comparatively high value of x , the remaining particles must have a lesser energy, leading to the fact that the particle under consideration has itself a lesser average kinetic energy than if no particle were present at that height.

To analyse this problem, we start from the *conditional* probability that a particle has momentum \vec{p}_0 given that it is at height x_0 . This is given by

$$\rho(\vec{p}_0|x_0) \propto \Omega_{N-1} \left(E - q\mathcal{E}x_0 - \frac{p_0^2}{2m} \right). \quad (8)$$

Here Ω_{N-1} is the volume of the energy surface for $N - 1$ particles. The argument of Ω_{N-1} reflects the fact that the remaining energy is in the observed particle. The proportionality factor is independent of \vec{p}_0 and x_0 , and so does not matter.

We thus have:

$$\begin{aligned}
\ln \rho(\vec{p}_0|x_0) &= \ln \Omega_{N-1} \left(E - q\mathcal{E}x_0 - \frac{p_0^2}{2m} \right) - \ln \Omega_{N-1}(E) + K \\
&\approx K - \left(q\mathcal{E}x_0 + \frac{p_0^2}{2m} \right) \frac{\partial}{\partial E} \ln \Omega_N(E) + \frac{1}{2} \left(q\mathcal{E}x_0 + \frac{p_0^2}{2m} \right)^2 \frac{\partial^2}{\partial E^2} \ln \Omega_N(E) \\
&= K' - \frac{p_0^2}{2mk_B T_M} - \frac{1}{2C_V k_B T_M^2} \left(q\mathcal{E}x_0 + \frac{p_0^2}{2m} \right)^2 \\
&= K'' - \frac{p_0^2}{2mk_B T_M} \left(1 + \frac{q\mathcal{E}x_0}{C_V T_M} \right) - \frac{p_0^4}{8m^2 C_V k_B T_M^2}. \tag{9}
\end{aligned}$$

Note that in the third line we have discarded an additive constant depending only on x_0 , since we want the \vec{p}_0 dependence of $\rho(\vec{p}_0|x_0)$ at fixed x_0 . Here T_M is the microcanonical temperature and C_V is the heat capacity at constant volume of the whole system, which is therefore proportional to the number of particles N . This shows that the kinetic temperature $T_K(x_0)$ as a function of x_0 is given by

$$T_K(x_0) \approx T_M \left(1 - \frac{q\mathcal{E}x_0}{C_V T_M} \right). \tag{10}$$

From this follow both the apparently paradoxical claims made in the Introduction. Indeed, we see first that the kinetic temperature has a spatial variation. But we also see that the actual value of the gradient depends on q . If we thus have two different species with different charges, then at sufficient height, both species will have markedly different kinetic temperatures. Under such circumstances, particles of different species will not tend to have the same kinetic energy on the average, even though they interact with each other. See reference [6] for the numerical study of a model in which two such species of particles, of which one is charged and the other not, coexist. The constancy of the kinetic temperature of the neutral species is confirmed, as well as the kinetic temperature gradient for the charged species.

4 The zero'th law for long-range systems

Finally, we turn to the systems with long range interactions. The partition function of a broad class of systems having long-range interactions can be expressed in the form [13,14]

$$Z(\beta) = \int dm \exp[-N\beta f(\beta, m)]. \tag{11}$$

The free energy $\phi(\beta)$ is then given by

$$\phi(\beta) = \min_m f(\beta, m). \tag{12}$$

From this follows, by the definition of the Legendre transform, that the canonical entropy is given by

$$s_c(\epsilon) = \min_{\beta} \max_m [\beta f(\beta, m) - \beta\epsilon]. \tag{13}$$

On the other hand, the microcanonical partition function $\Omega(\epsilon)$ is given by

$$\begin{aligned}\Omega(\epsilon) &= \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} d\beta Z(\beta) e^{N\beta\epsilon} \\ &= \frac{1}{2\pi i} \int dm \int_{-i\infty}^{i\infty} d\beta \exp[-N(\beta f(\beta, m) - \beta\epsilon)].\end{aligned}\quad (14)$$

Here $\epsilon = E/N$ is the energy per particle.

Considering that a minimum of an analytic function along the real axis corresponds to a maximum along the imaginary axis, we are led [14] to the following expression for the microcanonical entropy

$$s_m(\epsilon) = \min_m \max_{\beta} [\beta f(\beta, m) - \beta\epsilon]. \quad (15)$$

The concavity of $s_c(\epsilon)$ follows from the fact that it is given by the minimum over β of a set of functions linear in ϵ , see (13). On the other hand, the microcanonical entropy is not necessarily concave, since it is defined, by (15), as a minimum (over m) of functions that, by the same token, are *convex* in ϵ . But this does not allow to draw any conclusions concerning $s_m(\epsilon)$. Indeed, the non-concavity of entropy is equivalent to the well-known phenomenon of negative specific heat, which was reviewed by Lynden-Bell in [15] and discussed numerically for metal clusters, for example, in [16].

It is also readily follows from (13, 15) that $s_m(\epsilon) \leq s_c(\epsilon)$, which is compatible with the intuition that $s_m(\epsilon)$ corresponds to the entropy of a restricted system, so that lifting the restriction of fixed energy may lead to a spontaneous evolution of the system.

Let us now consider two identical copies of a system at a value ϵ_0 at which $s_m(\epsilon)$ is not concave. Let us allow the two systems to exchange energy, maintaining the total energy of the composite system constant all the while. The composite system can thus be described by the energies per particle of both subsystems, given by $\epsilon_0 - \delta$ and $\epsilon_0 + \delta$, as follows from the fact that the total system remains at constant total energy. The entropy of the compound system is then given by

$$s_m^{(comp)}(\delta) = \frac{1}{2} [s_m(\epsilon_0 + \delta) + s_m(\epsilon_0 - \delta)]. \quad (16)$$

If ϵ_0 is such that the entropy $s_m(\epsilon)$ is non-concave (convex) around $\epsilon = \epsilon_0$, it follows that $s_m^{(comp)}(\delta)$ has a *minimum* at $\delta = 0$, so that the system spontaneously evolves to a state in which the two subsystems differ.

In references [10, 11] this effect was confirmed in the system

$$H = \sum_{i=1}^N \frac{p_i^2}{2} - \frac{J}{2N} \sum_{i,j=1}^N \cos(\theta_i - \theta_j) - K \sum_{i=1}^N \cos(\theta_{i+1} - \theta_i), \quad (17)$$

which represents an *XY*-model in one dimension, with a ferromagnetic long-range interaction and a nearest-neighbour interaction. For this model the function $f(\beta, m)$ exists and can be evaluated [17] explicitly³. The model has a tricritical point for some $K < 0$, and close to it, we have a region with negative specific heat.

³ Well, more or less: it is defined as the largest eigenvalue of a linear integral operator with a kernel given by a modified Bessel function.

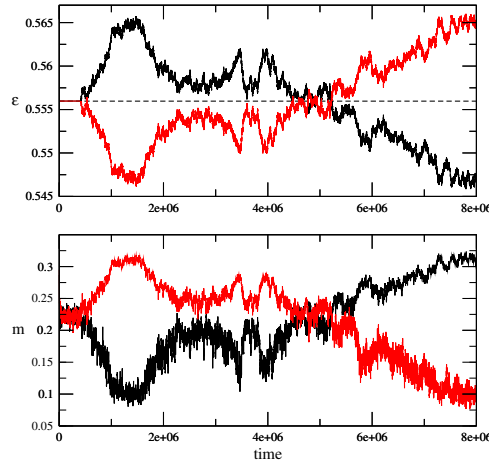


Fig. 1. Temporal evolution of energy density (top) and magnetization (bottom) of system 1 (black) and system 2 (red), using the momentum coupling $H_{int}^{(p)}$. The curves were obtained by averaging over a sliding time window. The values of parameters are $J = 1$, $K_1 = -0.178$, $N = 5000$, $\eta = 0.1$, $N_{int} = 10$, $\epsilon_0 = 0.55597$. Note how the 2 systems interchange roles due to finite size effects.

Let us now do what is described above: we take two copies of the system, with the same values of J , K , N and E , and couple them weakly in such a way as to allow for energy exchange between the two systems. We use the interaction

$$H_{int}^{(p)} = \eta \sum_{i=1}^{N_{int}} p_i^1 p_i^2, \quad (18)$$

where p_i^γ is the momentum of rotor i of system γ , $\eta > 0$ is the inter-system coupling constant and $N_{int} \ll N$ is the number of rotors that interact in both systems. The result of the corresponding molecular dynamics simulations (performed with a symplectic algorithm) is shown in Figure 1. We see that the system does indeed evolve spontaneously out of its initial state.

5 Conclusions

As we have seen, the apparently outlandish claims made in the Introduction can readily be sustained. They do not rely either on high-level mathematics nor do they arise from the consideration of highly special, pathological systems. Rather, once the analysis is understood, the reader's reaction may well be "Of course, if *that* was what you meant, it is not remarkable at all. In fact, after understanding it, I find it quite trivial".

That last statement is, almost by definition, correct. Nevertheless, the examples described above may serve as a set of cautionary situations in which the possibility of unexpected effects arises. Further, such situations may be useful if one wishes to *prove* with mathematical rigor, for example, that any system tends to thermodynamic equilibrium, or that identical systems remain in equilibrium when put in weak thermal contact. The proof must then take care to exclude in some way, examples as those described here.

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