

# The Spin-Echo System Reconsidered\*

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## Abstract

Simple models have played an important role in the discussion of foundational issues in statistical mechanics. Among them the spin-echo system is of particular interest since it can be realized experimentally. This has led to inferences being drawn about approaches to the foundations of statistical mechanics, particularly with respect to the use of coarse-graining. We examine these claims with the help of computer simulations.

## 1 Introduction

Kinetic equations are very useful in statistical mechanics but they are, in general, approximations to the behaviour of the underlying systems. Therefore, any conclusions which can be drawn from them are of limited significance for the resolution of foundational issues. What are needed are 'exact' results, or at least situations in which numerical errors do not affect qualitative behaviour. This is a severe restriction; most interesting problems in statistical mechanics concern cooperative systems and, even at equilibrium (see e.g. Baxter, 1982) there are few of these which can be solved exactly. So, of necessity, useful examples are of assemblies of non-interacting microsystems and the literature contains discussions of many 'toy models' of this kind, some stochastic and some deterministic. Simulations for a number of these are available in Lavis (2003); here we confine our attention to an assembly of magnetic dipoles precessing in a field. We shall investigate the time-evolution of the *Boltzmann entropy*, the fine-grained and coarse-grained versions of the *Gibbs entropy* and the magnetization. We reverse the dynamic evolution at an instant of time and demonstrate that the system returns to a state equivalent to that at the initial time. This is the *spin-echo effect*.

### 1.1 Forms of Entropy

Consider a system, which at time  $t$  has a microstate given by the vector  $\mathbf{x}(t)$  in the *phase-space*  $\Gamma$ . Some autonomous dynamics  $\mathbf{x} \rightarrow \phi_t \mathbf{x}$ , ( $t \geq 0$ ) determines a *flow* in  $\Gamma$  and the set of points  $\mathbf{x}(t) = \phi_t \mathbf{x}(0)$ , parameterized by  $t \geq 0$ , gives a *trajectory*. The set of mappings  $\{\phi_t\}_{t \geq 0}$  is a semi-group. The system is *reversible* if there exists a self-inverse operator  $\mathcal{J}$  on the points of  $\Gamma$ , such that  $\phi_t \mathbf{x} = \mathbf{x}'$

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\*Published (with some typing errors) in *Foundations of Physics*, **34**, 669–688 (2004).

implies that  $\phi_t \mathfrak{J} \mathbf{x}' = \mathfrak{J} \mathbf{x}$ . Then  $\phi_{-t} = (\phi_t)^{-1} = \mathfrak{J} \phi_t \mathfrak{J}$  and the set  $\{\phi_t\}$  with  $t \in \mathbb{R}$  or  $\mathbb{Z}$  is a group.

### 1.1.1 The Boltzmann Entropy

Macrostates (observable states) are defined by a set  $\Xi$  of macroscopic variables.<sup>1</sup> Let the set of macrostates be  $\{\mu\}_\Xi$ . They are so defined that every  $\mathbf{x} \in \Gamma$  is in exactly one macrostate denoted by  $\mu(\mathbf{x})$  and the mapping  $\mathbf{x} \rightarrow \mu(\mathbf{x})$  is many-one. Every macrostate  $\mu$  is associated with its ‘volume’  $\mathcal{V}_\Xi(\mu)$  in  $\Gamma$ .<sup>2</sup> We thus have the map  $\mathbf{x} \rightarrow \mu(\mathbf{x}) \rightarrow \mathcal{V}_\Xi(\mathbf{x}) \equiv \mathcal{V}_\Xi(\mu(\mathbf{x}))$  from  $\Gamma$  to  $\mathbb{R}^+$  or  $\mathbb{N}$ . The *Boltzmann entropy* is defined by

$$S_B(\mathbf{x}) = k_B \ln[\mathcal{V}_\Xi(\mathbf{x})]. \quad (1)$$

This is a phase function depending on the choice of macroscopic variables  $\Xi$ .

Suppose the system consists of  $N$  identical microsystems.<sup>3</sup> Then  $\Gamma_N$  is the direct product of  $N$  copies of  $\Gamma_1$ , the phase-space of one microsystem. Let  $\tilde{\mathbf{x}}^{(i)}(t)$  be the phase vector of the  $i$ -th microsystem moving in its  $\Gamma_1$ . Now divide  $\Gamma_1$  into an enumerable set of cells  $\gamma_k$  of equal volume  $\nu$  such that every point in  $\Gamma_1$  belongs to exactly one  $\gamma_k$ . The macroscopic variables  $\Xi$  are taken to be the set  $\{N_k\}$  of *coarse-graining variables*, where  $N_k$  is the number of microsystems with phase-points in  $\gamma_k$ . Then a macrostate is the part of  $\Gamma_N$  corresponding to a fixed set of values of  $\{N_k\}$  and

$$\mathcal{V}_{\{N_k\}}(\mathbf{x}) = \Omega(\{N_k(\mathbf{x})\})\nu^N, \quad \Omega(\{N_k\}) = \frac{N!}{\prod_k (N_k)!}, \quad (2)$$

$$S_B(\mathbf{x}) = k_B \ln[\Omega(\{N_k(\mathbf{x})\})] + k_B N \ln(\nu). \quad (3)$$

This formula is valid irrespective of whether the microsystems are interacting. However, if they are, then constraints will apply to the possible values of  $\{N_k\}$ .<sup>4</sup>

### 1.1.2 The Gibbs Entropy

The fine-grained Gibbs entropy<sup>5</sup> is given by the functional

$$S_{\text{FGG}}[\rho_N(t)] = -k_B \int_{\Gamma_N} \rho_N(\mathbf{x}; t) \ln\{\rho_N(\mathbf{x}; t)\} d\Gamma_N. \quad (4)$$

of the fine-grained probability density function  $\rho_N(\mathbf{x}; t)$  on  $\Gamma_N$ . For a measure-preserving system for which  $\rho_N(\mathbf{x}; t)$  satisfies Liouville’s equation  $S_{\text{FGG}}[\rho_N(t)]$  remains constant with time, as we shall demonstrate explicitly for the spin system in Sec. 2. The resolution to this problem suggested by Gibbs (1902, p. 148) (see also Ehrenfest and Ehrenfest-Afanassjewa, 1912) is to coarse-grain the

<sup>1</sup>These may include some thermodynamic variables (volume, number of particles etc.) but they will also include other variables, specifying, for example, the number of particles in a set of subvolumes. Ridderbos (2002) denotes these by the collective name of *supra-thermodynamic variables*.

<sup>2</sup>The term ‘volume’ being taken to mean some appropriate measure on  $\Gamma$ .

<sup>3</sup>In indication of which we denote the phase-space by  $\Gamma_N$ .

<sup>4</sup>Representing, for example, the condition that the phase point of the whole system must lie on an energy hypersurface in  $\Gamma_N$ .

<sup>5</sup>The ‘fine-grained’ qualification to the Gibbs entropy and probability density function is a convenient distinction from the coarse-grained versions defined below.

phase-space  $\Gamma_N$ , in the manner in which macrostates have been obtained in the Boltzmann approach. We first note that for a system of identical non-interacting microsystems the probability density function factorizes into a product of single-microsystem densities.

$$\rho_N(\mathbf{x}; t) = \prod_{i=1}^N \rho_1(\dot{\mathbf{x}}^{(i)}; t). \quad (5)$$

Then

$$S_{\text{FGG}}[\rho_N(t)] = -k_B N \int_{\Gamma_1} \rho_1(\dot{\mathbf{x}}; t) \ln\{\rho_1(\dot{\mathbf{x}}; t)\} d\Gamma_1. \quad (6)$$

Using the cells  $\gamma_k$  defined in Sec. 1.1.1 we define the coarse-grained probability density by

$$\tilde{\rho}_1(k; t) = \int_{\gamma_k} \rho_1(\dot{\mathbf{x}}; t) d\Gamma_1 \quad (7)$$

and the coarse-grained Gibbs entropy by

$$S_{\text{CGG}}[\tilde{\rho}_N(t)] = -k_B N \sum_k \tilde{\rho}_1(k; t) \ln\{\tilde{\rho}_1(k; t)\} + k_B N \ln(\nu). \quad (8)$$

The second term in (8) is required for consistency with the fine-grained entropy in the case where the fine-grained density is uniform (with possibly different values) over each of the cells. Then, from (7),  $\tilde{\rho}_1(k; t) = \nu \rho_1(\dot{\mathbf{x}}_k; t)$ , where  $\dot{\mathbf{x}}_k$  is any point in  $\gamma_k$  and substituting into (6) gives (8).<sup>6</sup>

If we begin with any fine-grained density  $\rho_N(\mathbf{x}; t)$  and calculate  $S_{\text{FGG}}[\rho_N(t)]$ , and then apply coarse-graining and calculate  $S_{\text{CGG}}[\tilde{\rho}_N(t)]$ ,

$$S_{\text{FGG}}[\rho_N(t)] \leq S_{\text{CGG}}[\tilde{\rho}_N(t)], \quad (9)$$

with equality only if the fine-grained density is uniform over the cells of the coarse-graining. Now we can conceive of two possible ways of tracing the evolution of entropy in the Gibbs coarse-grained picture.

- (i) We could begin with some fine-grained density giving entropy  $S_{\text{FGG}}[\rho_N(0)]$  at  $t = 0$  and watch its evolution as time increases. If at time  $t' \geq 0$  we coarse-grain, then

$$S_{\text{FGG}}[\rho_N(0)] = S_{\text{FGG}}[\rho_N(t')] \leq S_{\text{CGG}}[\tilde{\rho}_N(t')]. \quad (10)$$

However if we coarse-grain at two instants  $0 \leq t' < t''$  it is not necessarily the case that

$$S_{\text{CGG}}[\tilde{\rho}_N(t')] \leq S_{\text{CGG}}[\tilde{\rho}_N(t'')]. \quad (11)$$

The coarse-grained entropy will not necessarily show monotonic increase. However, the graph of the coarse-grained entropy will not depend on the instants at which coarse-graining is applied.

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<sup>6</sup>Alternatively the final term in (8) could be absorbed if the formula were written in the form of an integral (rather than summation) over the piecewise constant coarse-grained density.

- (ii) If, instead of the strategy adopted in (i) we coarse-grain at  $t'$  then follow the evolution of the coarse-grained density and then *re-coarse-grain* at the later time  $t''$ , (11) will hold. Coarse-grained entropy will show monotonic increase. However, the graph of entropy against time will be affected by the instances at which coarse-graining is applied.

From (2)–(3), using Stirling’s formula for large  $N$ ,<sup>7</sup>

$$S_B(\mathbf{x}) \simeq -k_B N \sum_k \frac{N_k(\mathbf{x})}{N} \ln \left( \frac{N_k(\mathbf{x})}{N} \right) + k_B N \ln(\nu). \quad (12)$$

The relationship between (8) and (12) is now easy to see. If on the one hand a very large assembly of microsystems is taken with initial density in  $\Gamma_1$  of  $N\rho_1(\mathbf{x};0)$  then  $N_k(t)/N$ , the proportion of the assembly in cell  $\gamma_k$  at time  $t$  is  $\tilde{\rho}_1(k;t)$  given by (7) and (12) is asymptotically equivalent to (8). Conversely, if in the Gibbs formulation the initial density function is chosen to be a set of  $N$  suitably-weighted Dirac delta functions, we recover (12). In summary, we expect the Boltzmann entropy in the limit of large  $N$  and close to the uniform distribution to converge to the coarse-grained Gibbs entropy.

## 2 The Model

Consider the simple model in which a magnetic dipole of moment  $\mathbf{m}$  is fixed at its centre but is free to rotate in the presence of a constant magnetic field  $\mathbf{B}$ . The equation of motion of the dipole will be

$$\dot{\mathbf{m}}(t) = g \mathbf{m}(t) \wedge \mathbf{B}, \quad (13)$$

where  $g$  is the gyromagnetic ratio. Released from rest the dipole will precess at a constant angle to  $\mathbf{B}$ . In particular, if  $\mathbf{m}$  is located at the origin of a cartesian coordinate system with  $\mathbf{B}$  in the direction of the negative  $z$ -axis and if initially  $\mathbf{m}$  lies in the  $x - y$  plane, its subsequent motion remains in the  $x - y$  plane and is given by

$$\mathbf{m}(t) = (m \cos(\theta(t)), m \sin(\theta(t))), \quad (14)$$

where

$$\theta(t) = \phi_t \theta(0) = \mathcal{F}_{2\pi}(\theta(0) + \omega t), \quad \omega = Bg, \quad (15)$$

and<sup>8</sup>

$$\mathcal{F}_\alpha(x) = \alpha \times \text{Non-Integer Part} \left( \frac{x}{\alpha} \right). \quad (16)$$

Suppose that at some time  $t = \tau$  the magnetic field  $\mathbf{B}$  is turned off and a field  $\mathbf{B}'$ , in the direction of the  $x$ -axis is turned on for a time  $t' = \pi/B'g$ . The effect of this will be to rotate the dipole through an angle  $\pi$  about the  $x$ -axis, translating its position from  $\theta(\tau) = \mathcal{F}_{2\pi}(\theta(0) + \omega\tau)$  to  $\theta'(\tau) = 2\pi - \mathcal{F}_{2\pi}(\theta(0) + \omega\tau) =$

<sup>7</sup>In fact the approximation is close only when not only  $N$ , but all the  $N_k$  are large. This means that it is good only for large  $N$  and a distribution of microsystems close to the uniform distribution over the cells.

<sup>8</sup>Where, of course,  $\mathcal{F}_\alpha(x \pm \mathcal{F}_\alpha(y)) = \mathcal{F}_\alpha(x \pm y)$ , for all real  $x$  and  $y$  and positive  $\alpha$ .

$\mathcal{F}_{2\pi}(2\pi - \theta(0) - \omega\tau)$ ; a reflection in the  $x$ -axis. We denote this self-inverse reflection operator by  $\mathfrak{R}$ ; that is  $\mathfrak{R}(\theta, \omega) = (2\pi - \theta, \omega)$ . With reflection applied at  $t = \tau$

$$\theta(2\tau) = \mathcal{F}_{2\pi}(\theta'(\tau) + \omega\tau) = 2\pi - \theta(0). \quad (17)$$

This reflectional return or *echo-effect* is what gives the system its name. The model is also reversible with  $\mathfrak{I}(\theta, \omega) = (\theta, -\omega)$ . Then

$$\theta(2\tau) = \phi_{-\tau}\theta(\tau) = \mathcal{F}_{2\pi}(\theta(\tau) - \omega\tau) = \theta(0). \quad (18)$$

So the system has two mechanisms for making it ‘retrace its steps’. However, this is not so strange. It would be true for any system with periodic boundary conditions; and a similar effect occurs when a particle is in one-dimensional motion at constant speed  $v$  confined between elastic walls at  $x = 0$  and  $x = L$ . Then we can ‘unfold’ right-to-left motions of the particle into the region  $[L, 2L]$ . The model is now equivalent to the dipole motion with  $\pi$  replaced by  $L$ . The echo transformation  $x \rightarrow 2L - x$  at  $t = \tau$  is now *exactly the same as* reversing the direction of the velocity, with  $x(2\tau) = x(0)$  and  $\dot{x}(2\tau) = -\dot{x}(0)$ . However, there is a second possible transformation  $x \rightarrow L - x$ . Now  $x(2\tau) = L - x(0)$  and  $\dot{x}(2\tau) = \dot{x}(0)$ . For an assembly of particles this fulfills the purposes of the echo transformation just as well.<sup>9</sup>

As indicated, our interest is in an assembly of microsystems. Consider the collection  $\mathbf{m}^{(i)}$ ,  $i = 1, 2, \dots, N$  of such dipoles with angular velocities  $\omega^{(i)}$  in the range  $[\omega_{\min}, \omega_{\max}]$  and plot their evolutions in the  $\theta - \omega$  plane. Suppose that,  $N = 500$ ,  $\tau = 100$ ,  $\omega_{\min} = 0.75$  and  $\omega_{\max} = 1.25$  and that the  $\omega^{(i)}$  are chosen randomly from a uniform distribution on  $[\omega_{\min}, \omega_{\max}]$  with  $\theta(0) = 0$  for all the dipoles. Then we have the situation shown in Fig. 1. At  $t = 0$  each dipole is aligned in the  $\theta = 0$  direction and at  $t = 5$  the phase-points in  $\Gamma_1$  form lines with this effect persisting to about  $t = 50$ . After this the periodic boundary conditions lead to a breakup of the ordered appearance and a ‘spreading’ of phase-points in  $\Gamma_1$ . When the reflectional transformation is applied at  $t = \tau = 100$  the distribution of phase-points at  $t > \tau$  is the mirror image in  $\theta = \pi$  of its form at  $2\tau - t$  and the final configuration is along the line  $\theta = 2\pi$  at  $t = 2\tau$ . A macroscopic variable which can be used to follow the evolution of the system is the  $x$  component of the magnetization density

$$\sigma(t) = \frac{1}{mN} \sum_{i=1}^N \mathbf{m}^{(i)}(t) \cdot \hat{\mathbf{x}} = \frac{1}{N} \sum_{i=1}^N \cos(\theta^{(i)}(t)). \quad (19)$$

This is shown in Fig. 2. There is a rapid decrease of magnetization density from its initial value of unity to fluctuations around the perfectly spread value of  $\sigma = 0$ . The average magnitude of these fluctuations will be inversely proportional to  $N$  and in general we expect them to be quite small. Since the angular velocities have been chosen randomly the assembly is quasi-periodic. It is also volume-preserving and will, therefore, satisfy the Poincaré (1890) recurrence theorem. For ‘most’ initial points, if there is no echo reflection, the phase point  $(\boldsymbol{\theta}, \boldsymbol{\omega}) = (\theta^{(1)}, \dots, \theta^{(N)}, \omega^{(1)}, \dots, \omega^{(N)})$  in the  $2N$ -dimensional phase-space  $\Gamma_N$  nevertheless returns to within a neighbourhood of its initial value.<sup>10</sup> This will

<sup>9</sup>It undoes during the time interval  $[\tau, 2\tau]$  the spreading which has occurred during the interval  $[0, \tau]$ .

<sup>10</sup>The recurrence time will, of course, be dependent on the size of the neighbourhood.

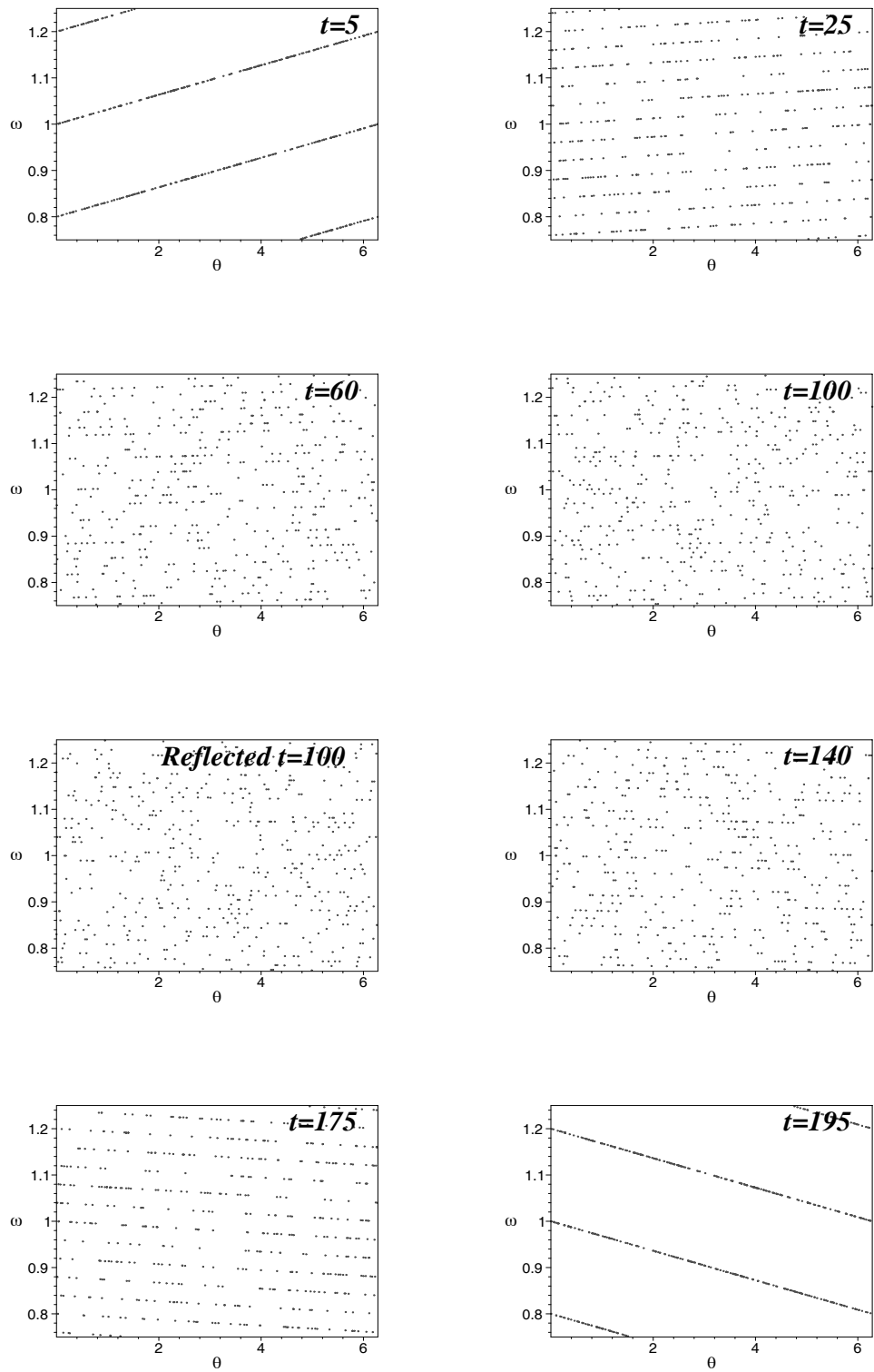


Figure 1: An assembly of  $N = 500$  rotating dipoles.

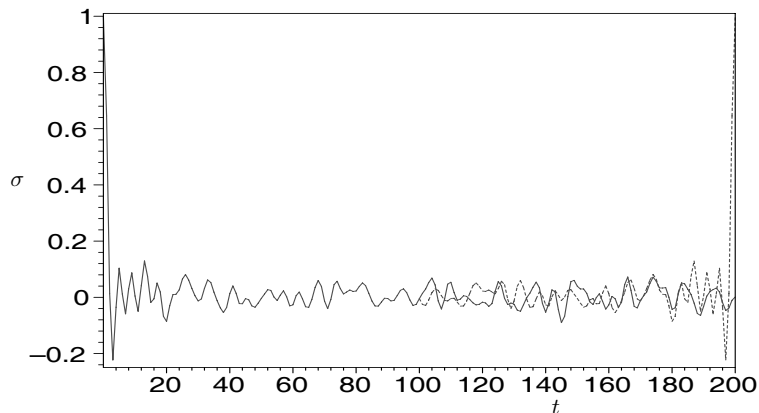


Figure 2: The evolution of the magnetization density. After  $t = \tau = 100$  the broken line gives the echo.

lead to a large fluctuation in magnetization density. Of course, if the initial angular velocities are chosen to be commensurate, the system will be periodic and will return exactly to its initial point with  $\sigma = 1$ .

There would be nothing particularly special about this model, if it were not for the fact that it has been realized experimentally. Hahn (1950) (see also Hahn, 1953; Rhim et al., 1971; Brewer and Hahn, 1984) applied a magnetic field to various liquids whose molecules contain hydrogen atoms. By manipulating the components of the magnetic field he was able to start with the dipole moments of the proton spins in the  $x$ -direction, make them precess around the  $z$ -axis and then reflect the directions of the dipoles in the  $x$ -axis to achieve the echo effect with the dipoles returning to their initial alignment.<sup>11</sup> This system has aroused some interest in relation to questions of reversibility in statistical mechanics (Blatt, 1959; Mayer and Mayer, 1977; Denbigh and Denbigh, 1985; Ridderbos and Redhead, 1998; Ridderbos, 2002). This will be discussed in Sec. 3. Here we shall simply present the results of our calculations.

The cells to be used both for the Boltzmann entropy and the coarse-grained Gibbs entropy are defined by dividing the single-dipole phase-space  $\Gamma_1$  into  $n_\theta \times n_\omega$  rectangles with edges parallel to the  $\theta$  and  $\omega$  axes and of lengths  $\Delta\theta = 2\pi/n_\theta$  and  $\Delta\omega = (\omega_{\max} - \omega_{\min})/n_\omega$  respectively. In Fig. 3, we show the scaled Boltzmann entropy

$$\bar{S}_B(\mathbf{x}(t)) = \frac{S_B(\mathbf{x}(t)) - (S_B)_{\min}}{(S_B)_{\max} - (S_B)_{\min}}, \quad (20)$$

for the same evolution as Fig. 1, and  $n_\theta = n_\omega = 100$ , where  $(S_B)_{\min} = k_B N \ln(\Delta\theta\Delta\omega)$  is the entropy were all the spins to be concentrated in one cell and  $(S_B)_{\max}$  corresponds to the spins being equally distributed over the cells.<sup>12</sup> The continuous and broken lines for  $t > 100$  correspond respectively to

<sup>11</sup>The variations in the angular velocities were achieved from small variations in the strength of the magnetic field throughout the sample.

<sup>12</sup>We do not, of course, imply that these scaling factors correspond to attainable states for the system, since the distribution of angular velocities is invariant with time.

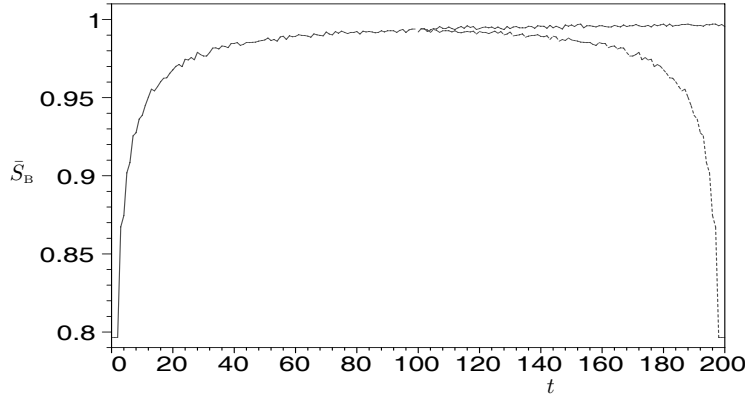


Figure 3: The evolution of the Boltzmann entropy of the dipole assembly. After  $t = \tau = 100$  the broken line gives the echo.

the evolutions without and with the echo-effect.

We now calculate the fine-grained Gibbs entropy. Suppose that the initial probability density function is concentrated and uniform over the rectangle  $\omega \in [\omega_{\min}, \omega_{\max}]$ ,  $\theta \in [0, \theta_0]$ , ( $\theta_0 < 2\pi$ ). Then

$$\rho_1(\theta, \omega; 0) = \frac{\mathcal{H}(\theta) - \mathcal{H}(\theta - \theta_0)}{\theta_0(\omega_{\max} - \omega_{\min})}, \quad (21)$$

where  $\mathcal{H}(\theta)$  is the *Heaviside unit function*, and

$$\rho_1(\theta, \omega; t) = \begin{cases} \frac{\mathcal{H}(\theta - \mathcal{F}_{2\pi}(\omega t)) - \mathcal{H}(\theta - \mathcal{F}_{2\pi}(\theta_0 + \omega t))}{\theta_0(\omega_{\max} - \omega_{\min})}, & \mathcal{F}_{2\pi}(\omega t) < \mathcal{F}_{2\pi}(\theta_0 + \omega t), \\ \frac{\mathcal{H}(\theta - \mathcal{F}_{2\pi}(\omega t)) - \mathcal{H}(\theta - \mathcal{F}_{2\pi}(\theta_0 + \omega t)) + \mathcal{H}(\theta) - \mathcal{H}(\theta - 2\pi)}{\theta_0(\omega_{\max} - \omega_{\min})}, & \mathcal{F}_{2\pi}(\theta_0 + \omega t) < \mathcal{F}_{2\pi}(\omega t). \end{cases} \quad (22)$$

If the echo transformation  $\theta \rightarrow 2\pi - \theta$  is applied at the time  $\tau$  the one-spin probability density function for  $t > \tau$  is given, in terms of (22) by  $\rho_1(2\pi - \theta, \omega; 2\tau - t)$ . The evolution of this fine-grained probability density function, with  $\tau = 100$ , is shown in Fig. 4. Over the time interval  $[0, \tau]$  the cross-hatched region spreads itself in ever-thinner striations over  $\Gamma_1$  and this process would continue if the echo transformation were not applied.<sup>13</sup> The effect of the echo-transformation is as in Fig. 1; it produces a configuration at  $t > \tau$  which is the reflection in  $\theta = \pi$  of the configuration at  $2\tau - t$ . Substituting from (22) into (6) gives

$$S_{\text{FGG}}[\rho_N(t)] = k_B N \ln\{\theta_0(\omega_{\max} - \omega_{\min})\}. \quad (23)$$

<sup>13</sup>However, we have to be a little cautious about this since we are considering a collection of non-interacting dipoles. For each dipole the second equation of motion to pair with (15) is  $\omega(t) = \omega(0)$ . Motion is horizontal in  $\Gamma_1$  and, unlike for example a gas of particles moving according to the baker's transformation (Lavis, 2003), and contrary to the assertion by Ridderbos and Redhead (1998, p. 1248) the system is *mixing* in  $\Gamma_1$  only in a limited sense.



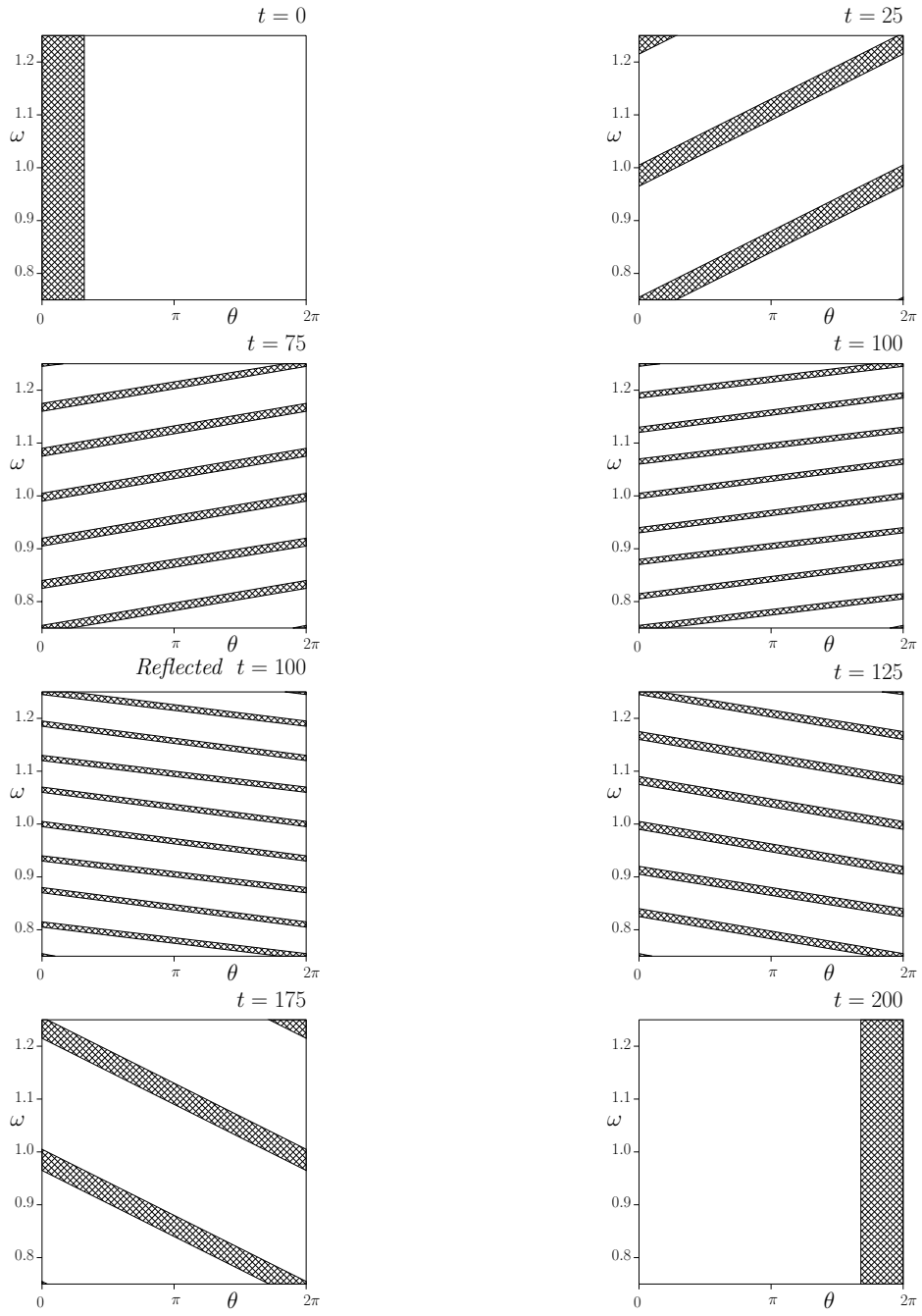


Figure 4: The evolution of the fine-grained one-dipole probability density function with the echo occurring at  $t = \tau = 100$ .

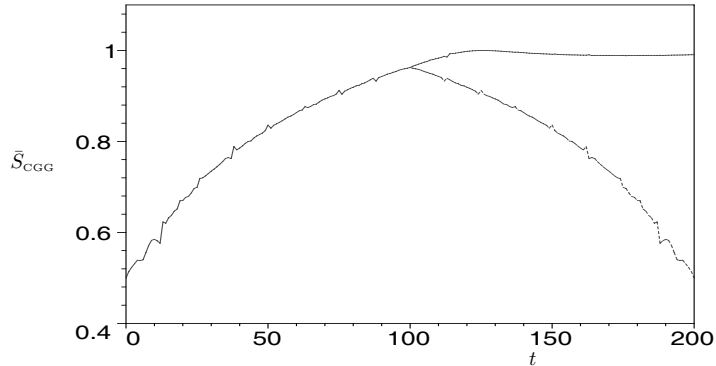


Figure 5: The evolution of the coarse-grained Gibbs entropy of the dipole assembly. After  $t = \tau = 100$  the broken line corresponds to the echo.

This is simply an expression of the well-known result that the fine-grained Gibbs entropy is invariant with respect to time. The coarse-grained Gibbs entropy is now calculated using the same coarse-graining as was used to obtain the macrostates for the Boltzmann entropy.  $S_{CGG}[\tilde{\rho}_N(t)]$  will have a maximum value when the cross-hatched area in Fig. 4 is spread evenly over the cells. Then  $\tilde{\rho}_1(k; t) = (\Delta\theta\Delta\omega)/\{2\pi(\omega_{\max} - \omega_{\min})\}$ . Substituting into (8) (with  $\nu = \Delta\theta\Delta\omega$ ) gives

$$(S_{CGG})_{\max} = k_B N \ln\{2\pi(\omega_{\max} - \omega_{\min})\}. \quad (24)$$

We adopt the strategy (i) of Sec. 1.1.2 and coarse-grain the fine-grained density as time evolves (rather than performing successive re-coarse-grainings). The results for  $\bar{S}_{CGG}[\tilde{\rho}_N(t)] = S_{CGG}[\tilde{\rho}_N(t)]/(S_{CGG})_{\max}$ , when  $n_\theta = n_\omega = 100$ , are shown in Fig. 5.

Ridderbos and Redhead (1998) have shown that the coarse-grained entropy tends to its maximum value (24) as  $t \rightarrow \infty$  and our simulations in Fig. 5 support this result.

### 3 Discussion

The first discussion of the spin-echo effect in relation to coarse-graining is due to Blatt (1959). His argument is that “the coarse-graining approach depends crucially upon the assertion that ‘fine-grained’ measurements are impracticable, and thus [that] the fine-grained entropy is a meaningless concept” (p. 746). Since a counter-example to this is provided by the spin-echo system which shows that “macroscopic observers are not restricted to coarse-grained experiments” he concludes that it “is not permissible to base fundamental arguments in statistical mechanics on coarse-graining” (p. 749). So what is the weight of this argument? It is based on ingenious experiments which allow a system of independent microsystems to be returned, by macroscopic means, to a phase state close to the one they were in at an earlier time. Two effects could account for

‘closeness’ rather than exact return. The first would be an internal cooperative effect, in this case a spin–spin coupling.<sup>14</sup> Blatt (1959, p. 750) remarks that the decrease in the echo–pulse arising from this is “from [the] present point of view accidental”. He is content to consider a system of independent microsystems, because in any event the inclusion of cooperative effects would not allow an escape from the iron hand of Liouville’s theorem; the fine-grained Gibbs entropy would still be constant. He is interested in the external (spin–lattice) source of the deviation from exact return. This interventionist alternative to coarse-graining, which is also the position of Ridderbos and Redhead (1998) and Ridderbos (2002) will not be discussed here. Rather we return to the original contention that the demonstration of a system which can be controlled more-or-less exactly at the microscopic level by macroscopic means is the death-blow for coarse-graining. Of course, the coarse-graining referred to by Blatt (and also by Ridderbos and Redhead and Ridderbos) is of the Gibbs–Ehrenfest type and it is true that Tolman (1938, p. 167) in justifying this argues that “in making any actual measurement of the [macroscopic variables] of the system . . . we ordinarily do not achieve the precise knowledge of their values theoretically permitted by classical mechanics”. But if this were the main argument for coarse-graining of the Gibbs–Ehrenfest or Boltzmann kind it would be very weak. It has always been possible to obtain analytic solutions for assemblies of non-interacting microsystems and with the advent of fast computing we can, as we have here, produce data for assemblies of arbitrary size. The fact that such a system can be realized experimentally and controlled macroscopically may have been of great importance technically, but it is hardly a milestone in foundational development. In fact it is not clear that either Gibbs (1902) or Ehrenfest and Ehrenfest-Afanassjewa (1912) intended to justify the procedure by an appeal to the limitations of measurement. Gibbs (*ibid*, p. 148) refers to the cells of the coarse-graining as being “so small that [the fine-grained probability density function] may in general be regarded as sensibly constant within any one of them at the initial moment” and the Ehrenfests (*ibid*, p. 52) simply observe that the cells must be “small, but finite”. In the case of the Boltzmann entropy the situation is somewhat clearer. The size of the cells defines the ‘macro-scale’ as distinct from the ‘micro-scale’ (Lebowitz, 1993). Of course, this demarcation is to some extent arbitrary, but it is equally so for any macroscopic physical theory.<sup>15</sup> As is pointed out by Grünbaum (1975), Boltzmann’s entropy can be regarded as a measure of homogeneity and in this context the equilibrium state corresponds simply to the maximum entropy state, which has the most homogeneity. It is precisely and only here, in defining a measure for homogeneity at equilibrium (Ridderbos, 2002), that the demarcation between the macro- and micro-scales must be made. And this is unavoidable since no distribution of discrete points over a continuum is uniform on all scales.

We now consider the case made by Denbigh and Denbigh (1985, p. 49–50 and 140–143)<sup>16</sup> for the assertion that the spin–echo system exemplifies circumstances that are “highly exceptional” in reproducing the kind of reversible situation used by Loschmidt (1876) in his challenge to Boltzmann. The argument hinges on a comparison between a gas expanding in a box and the spin–echo system.

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<sup>14</sup>Similar experiments including dipolar coupling were performed by Rhim et al. (1971). Whilst these are of importance experimentally they do not affect the argument.

<sup>15</sup>See e.g. the definition of fluid density in Landau and Lifshitz (1959, p. 1).

<sup>16</sup>The same argument is reproduced in Ridderbos and Redhead (1998, p. 1253–1254).

This already presents some problems since, as we have shown in Sec. 2, the states of a particle moving in one dimension between perfectly reflecting barriers are isomorphic to those of a single spin precessing in a field with the spin-echo reflection equivalent to velocity inversion. It follows from this that non-interacting assemblies of each of these are isomorphic.<sup>17</sup> A summary of the situation considered by Denbigh and Denbigh (1985, p. 49–50) is as follows:<sup>18</sup>

- (i) Let  $A \rightarrow B$  be a “*macroscopic* process” from a thermodynamic state  $A$  to a thermodynamic state  $B$ .
- (ii) Let  $\mathcal{S}(A)$  and  $\mathcal{S}(B)$  be “those sets of exactly specified microstates which are accessible to the gas” in states  $A$  and  $B$ .
- (iii) Let  $\mathcal{I}\mathcal{S}(A)$  and  $\mathcal{I}\mathcal{S}(B)$  be those sets of macrostates obtained from  $\mathcal{S}(A)$  and  $\mathcal{S}(B)$  by reversing the velocities.
- (iv) If  $\mathbf{x}(0) \in \mathcal{S}(A)$  and  $\mathbf{x}(\tau) \in \mathcal{S}(B)$  then  $\mathcal{I}\mathbf{x}(\tau) \in \mathcal{I}\mathcal{S}(B)$  and  $\phi_\tau \mathcal{I}\mathbf{x}(\tau) = \mathcal{I}\mathbf{x}(0) \in \mathcal{I}\mathcal{S}(A)$ .

The inference is drawn that, if the system during the evolution  $\mathbf{x}(0) \rightarrow \mathbf{x}(\tau)$  goes from  $A$  to  $B$ , there is an allowed evolution  $\mathcal{I}\mathbf{x}(\tau) \rightarrow \mathcal{I}\mathbf{x}(0)$ , taking the system from  $B$  to  $A$ .<sup>19</sup> If thermodynamic entropy increases in one direction it will decrease in the other. This is the heart of Loschmidt’s paradox. In his reply to Loschmidt, Boltzmann (1877) pointed out that, whereas the trajectories from the majority of the points in  $\mathcal{S}(A)$  will yield an increase in entropy in the time interval  $[0, \tau]$ , only a small percentage of the points in  $\mathcal{I}\mathcal{S}(B)$  will yield trajectories giving a decrease in entropy over  $[0, \tau]$ . Denbigh and Denbigh (1985, p. 50) accept the general validity of this argument, but they believe that the spin-echo system where velocity inversion  $\mathcal{I}$  is replaced by reflection  $\mathcal{R}$  is a special case. They claim (translating into our notation) that “the situation [in the spin-echo system] is that the set of the type  $[\mathcal{R}\mathcal{S}(B)]$  contains the same number of members as the set of type  $[\mathcal{S}(A)]$ ; for every original spin there is a spin with a reversed velocity of precession”.<sup>20</sup> This statement contains two parts the first contentious and the second obviously true. It is certainly true that to every spin state there is another with the velocity of precession reversed (or the position reflected). A similar statement would be true for *any* reversible dynamic system. The distinguishing, although possibly not unique, feature of the spin system is that “these velocities can actually be reversed simultaneously by applying a magnetic pulse”. But this is a technical feature which could always be anticipated for a system of non-interacting microsystems. On the other hand if the first part of the statement (that  $\mathcal{R}\mathcal{S}(B)$  contains the

<sup>17</sup>It may be that Denbigh and Denbigh are effectively arguing that a two-dimensional gas of particles in a box  $\mathcal{B} = \{(x, y) | 0 \leq x \leq L, 0 \leq y \leq L\}$  where each particle moves at constant speed in the  $x$ -direction without any collisions is itself “highly exceptional”. If so the spin-echo system is irrelevant, except in so far as it is realized experimentally.

<sup>18</sup>They begin by referring to a gas of particles in a box where the operation needed to make the system retrace its steps is velocity reversion.

<sup>19</sup>There is one benign gap in this argument. It is assumed that the thermodynamic states for the reversed process are the same as those for the forward process. This is equivalent to supposing that, if  $\mathbf{x} \in \mathcal{S}(A)$ , then  $\mathcal{I}\mathbf{x} \in \mathcal{S}(A)$ . In other words,  $\mathcal{I}\mathcal{S}(A) \equiv \mathcal{S}(A)$ ,  $\mathcal{I}\mathcal{S}(B) \equiv \mathcal{S}(B)$ . The truth of these identities, although plausible, will, of course, depend on the meaning (yet to be discussed) of ‘accessible’.

<sup>20</sup>See also Ridderbos and Redhead (1998, p. 1254) for a similar assertion.

same number of members as  $\mathcal{S}(\mathcal{A})$ ) were true this would be in conflict with Boltzmann's answer to Loschmidt and it would be necessary to give an argument why this does not contradict the second law.<sup>21</sup> The problem with understanding this argument is in interpreting the term 'accessible'.<sup>22</sup> Let us suppose that it is to be interpreted as *all those microstates compatible with a given value for the  $x$  component of the magnetization  $mN\sigma(t)$* .<sup>23</sup> If initially  $\sigma(0) = 1$ , then all the spins must be aligned with the  $x$ -axis;  $\boldsymbol{\theta}(0) = (\theta^{(1)}(0), \dots, \theta^{(N)}(0)) = \mathbf{0}$  and the microstates  $\mathcal{S}(\mathcal{A})$  accessible to this macrostate  $\mathcal{A}$  correspond to all possible values of  $\boldsymbol{\omega} = (\omega^{(1)}, \dots, \omega^{(N)})$ . Now we have to define the final state  $\mathcal{B}$  at time  $t = \tau$ . We could simply take this to be given by  $\sigma(\tau) = 0$ . This would, of course, imply that  $\boldsymbol{\omega}$  is constrained by the condition

$$\sum_{i=1}^N \cos(\omega^{(i)}\tau) = 0. \quad (25)$$

This condition will eliminate most of the points in  $\mathcal{S}(\mathcal{A})$ . We have seen in Fig. 2 that a typical evolution of  $\sigma(t)$  starting from alignment in the  $x$  direction involves a rapid decrease followed by oscillations about  $\sigma = 0$ . A more realistic definition of  $\mathcal{B}$  is that  $\sigma$  lies in some small range  $[-\epsilon, \epsilon]$ . This replaces the condition (25) by

$$\left| \sum_{i=1}^N \cos(\omega^{(i)}\tau) \right| \leq \epsilon. \quad (26)$$

For sufficiently large  $\tau$  this condition will include 'most' of the points in  $\mathcal{S}(\mathcal{A})$ .<sup>24</sup> Now suppose we start at a phase point in  $\mathcal{S}(\mathcal{A})$  evolving into

$$\theta^{(i)}(\tau) = \mathcal{F}_{2\pi}(\omega^{(i)}\tau), \quad i = 1, 2, \dots, N \quad (27)$$

with

$$\left| \sum_{i=1}^N \cos(\theta^{(i)}(\tau)) \right| \leq \epsilon. \quad (28)$$

If we now apply the reflection  $\theta^{(i)}(\tau) \rightarrow 2\pi - \theta^{(i)}(\tau)$  the value of the sum on the left of (27) is unchanged. The new reflected phase point is also in  $\mathfrak{RS}(\mathcal{B}) \equiv \mathcal{S}(\mathcal{B})$  and, under the evolution<sup>25</sup>  $\phi_t(2\pi\mathbf{i} - \boldsymbol{\theta}, \boldsymbol{\omega})$ , over the further time interval  $[0, \tau]$  it returns to  $\mathfrak{RS}(\mathcal{A}) \equiv \mathcal{S}(\mathcal{A})$ . Most of the points of  $\mathcal{S}(\mathcal{A})$  satisfy this account, but the crucial question is whether in passing through  $\mathcal{S}(\mathcal{B})$  they include all (or even most) of the points of that set. The answer is clearly 'no'. To see this simply take a reflected point  $(2\pi\mathbf{i} - \boldsymbol{\theta}, \boldsymbol{\omega})$  which does return to  $\mathcal{S}(\mathcal{A})$  and apply any one of an infinity of small perturbations to the angular velocity. Most of these will not return to  $\mathcal{S}(\mathcal{A})$  in a time  $\tau$ , or in fact in any time interval much less than the Poincaré recurrence time.<sup>26</sup> This situation is shown in Fig. 6.

In his account of the spin-echo system Sklar (1993, p. 221) comments that

<sup>21</sup>Such an argument (again repeated by Ridderbos and Redhead (1998)) was provided by Mayer and Mayer (1977, p. 136).

<sup>22</sup>Ridderbos and Redhead (1998) use the term 'available' rather than 'accessible'.

<sup>23</sup>The argument could be suitably modified for variants on this definition, including a Boltzmann-like account base on macrostates.

<sup>24</sup>Those excluded will mostly be points where the angular velocities are commensurate and the motion is periodic.

<sup>25</sup>With  $\mathbf{i} = (1, 1, \dots, 1)$ .

<sup>26</sup>And even then we should need to broaden our definition of  $\mathcal{A}$  around  $\sigma = 1$ .

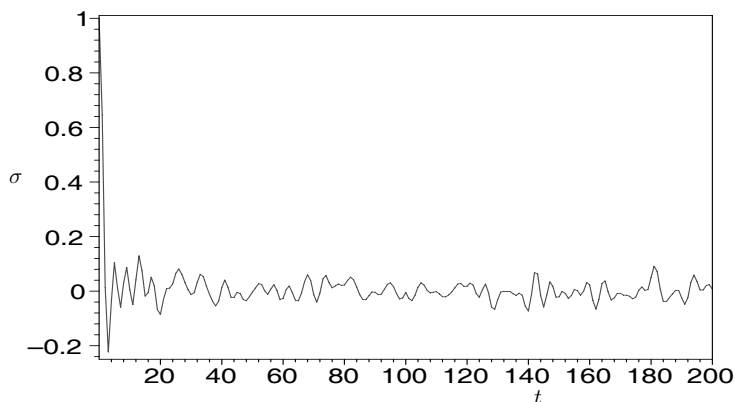


Figure 6: The evolution of the magnetization density. After  $t = 100$  the system is reflected and the angular velocities are subject to small perturbations.

“It is as if we could prepare a gas in such a way that an ensemble of gases so prepared would initially be uniformly spread throughout a box. But the overwhelming majority of the gases in the ensemble would then spontaneously flow to the left-hand half of the box.”

The problematic word in this quote is ‘prepare’. To prepare ‘from scratch’ a spin system or any other assembly in such a way that it will achieve a particular macrostate (low entropy, high magnetization, etc.) after a particular interval of time would involve careful adjustment of the relationships of velocities and positions for each microsystem; a task worthy of a *Maxwell demon*. However, what we have here is a much simpler process. We allow the system to achieve values which imply a recent memory of the required macrostate and then apply a reflection. This macroscopic operation by a *Loschmidt demon*<sup>27</sup> is only part of the process of preparation. The difficult part is left to the system.

The aim of the work of Ridderbos and Redhead (1998) is to use an examination of the spin-echo system to discredit the use of the Gibbs-Ehrenfest coarse-graining in favour of an interventionist approach. While it is true that the status of the coarse-grained Gibbs entropy lacks the clarity of the Boltzmann entropy it is by no means clear that the criticisms levelled at this approach by Ridderbos and Redhead (1998) are all valid. In Sec. 1.1.2 we described two methods for following the evolution of the coarse-grained Gibbs entropy, the first, involving a coarse-graining of the fine-grained distribution at each instant of time, and the second a sequence of re-coarse-graining as time progresses. The former, which is the standard understanding of the procedure (Denbigh and Denbigh, 1985, p. 55), does not yield a strict monotonic increase of entropy. However, it does allow the system to retrace its steps, either by velocity reversal or reflection (see Fig. 5). This is in conflict with the remarks of Ridderbos and Redhead (1998, p. 1250) that a “reversal of the dynamical evolution in the coarse-grained case does not cause the distribution to evolve back to its original form”. They appear to be thinking of the (obvious) impossibility of

<sup>27</sup>The term *Loschmidt demon*, seems to have been introduced by Rhim et al. (1971).

un-coarse-graining a coarse-grained distribution. The occurrence of the echo in these circumstances would certainly be “completely miraculous” (ibid, p. 1251), but this is not how coarse-grained evolution should be implemented. In any event, the more important question, raised by Ridderbos and Redhead (1998, p. 1251), is whether the spin–echo system is a “counterexample to the second law of thermodynamics”. The answer to this is surely that it depends on what you mean by the second law of thermodynamics. If, along with Maxwell and Boltzmann and probably the majority of physicists (see e.g. Ruelle, 1991, p. 113) entropy increase in an isolated system is taken to be highly probable but not certain, then the spin–echo model, along with simulations of other simple models (Lavis, 2003), is a nice example of the workings of the law. However, if entropy increase is an iron certainty this example is one, and not a special, example of a violation of the second law. Ridderbos and Redhead (1998, p. 1251) assert that the spin–echo experiments are not a violation of the second law because “we do not have a situation where a system evolves spontaneously from a high entropy state to a low entropy state.” Apart from the obvious conflict with the quote from Sklar given above, this, of course, depends on what you mean by “spontaneous”. Any experiment or simulation involves preparing the system in some initial state from which it evolves *spontaneously*. There is no conceptual reason why the system cannot be prepared in a state from which the entropy spontaneously decreases. It just difficult to do because of their relative paucity. As we have already indicated in our discussion the best way to find such a state is to let the system find it itself by evolving in the reverse direction. Then restarting the system in this state it will show a ‘spontaneous’ decrease in entropy.

## 4 Conclusions

We have considered the case made for the spin–echo experiments being an example of a special system which destroys the argument for using coarse-graining. We have argued that the reason for the Boltzmann version of coarse-graining has nothing to do with the inability to do fine-grained dynamic calculations,<sup>28</sup> or experiments, but is based on the necessity to have a demarkation between the micro- and macro-scales. The same arguments apply to Gibbs-Ehrenfest coarse-graining. The spin–echo experiments are of technical significance, particularly in respect of the fact that the echoing procedure can be effected by macroscopic means, but as a theoretical model of an assembly of non-interacting microsystems it is in no way special, as we have shown elsewhere (Lavis, 2003).

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<sup>28</sup>Indeed to calculate the Boltzmann entropy one needs the dynamic detail.

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