

# Statistical mechanics and thermodynamics of large and small systems

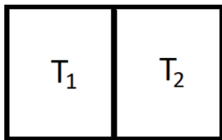
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- The notion of a thermal equilibrium state of an isolated macroscopic system ( $N \gg 1$  degrees of freedom) is basic to thermodynamics.
- Their existence is Postulate 1 in the Tisza-Callen formulation of thermodynamics.
- Thermodynamics further states that there is an extensive function called entropy  $S(E)$ , associated to such an equilibrium system which defines a temperature  $T = \left(\frac{\partial S}{\partial E}\right)^{-1} = \beta^{-1}$ ,  $S(E) \rightarrow S(T)$ .

- The “second law” says that this entropy will not decrease spontaneously when we remove a constraint from an equilibrium system, e.g., a partition between two isolated systems at different temperatures.



**Q1:** What does it mean for an individual closed macroscopic system to be in thermal equilibrium in terms of the “micro-state”, i.e., in terms of a phase point  $X$  in the phase space  $\Gamma$  of a classical system or a wave function  $\psi$  in the Hilbert space  $\mathcal{H}$  of a quantum system?

- Furthermore, how does one define the entropy for such an individual system and “derive”, or at least have a heuristic argument, for the observed irreversible behavior of macroscopic systems embedded in the second law when the microscopic dynamics (both classical and quantum) are reversible.

**Q2:** How to understand “thermal behavior” of small classical systems in contact with large thermal baths, the subject of stochastic thermodynamics, with a specific reference to a recent experiment by Bechhoefer, et al.

**Q3:** Thermal properties of subsystems of large and small “isolated” quantum systems.

- In classical mechanics, the microstate of a system of  $N$  particles confined to a region  $V$  in  $\mathbb{R}^d$  is a point  $X$  in the  $2dN$ -dimensional phase space.

$$X = (\vec{r}_1, \vec{p}_1, \dots, \vec{r}_N, \vec{p}_N), \quad \vec{r}_i \in V \subset \mathbb{R}^d, \quad \vec{p}_i \in \mathbb{R}^d$$

- A macroscopic system is one with “very large”  $N$ . We can then ask whether the system in a microstate  $X$  is in thermodynamic equilibrium.

- The time evolution  $X(t)$  of such an isolated classical system is given by the Hamiltonian equations of motion which leave the energy  $H(X) = E$ ,  $N$  and  $V$  unchanged.
- For  $X(t)$  to describe a system in equilibrium, it must then be true that all of its macroscopic properties remain, at least approximately, i.e. on a macroscopic scale, unchanged as a function of  $t$  (as long as the system stays isolated and the constraints remain in effect).

# Macrostates

- To describe the macroscopic state of a system of  $N$  atoms in a box  $\Lambda$ , say  $N \gtrsim 10^{20}$ , we make use of a much cruder description than that provided by the microstate  $X$ . We shall denote by  $M$  such a macroscopic description of a macrostate.
- As an example we may divide  $\Lambda$  into  $K$  cells, where  $K$  is large but still  $K \ll N$ , and specify the number of particles, the momentum and the amount of energy in each cell, with some tolerance.
- We denote by  $\Gamma_E$  a thin shell surrounding the surface  $H(X) = E$ .
- Clearly there are many  $X$ 's (in fact a continuum) which correspond to the same  $M$ . Let  $\Gamma_M$  be the region in  $\Gamma_E$  consisting of all microstates  $X$  corresponding to a given macrostate  $M$  and denote by  $|\Gamma_M|$  its Liouville volume.

- Generally in every  $\Gamma_E$  of a macroscopic system, there is one region  $\Gamma_M$  (possibly a few at a phase transition) which has most of the volume. This is called the equilibrium macrostate  $M_{eq}$ .

$$\frac{|\Gamma_{M_{eq}}|}{|\Gamma_E|} = 1 - \varepsilon \quad (1)$$

with  $\varepsilon \ll 1$ . When  $M(X)$  specifies a nonequilibrium state,  $|\Gamma_{M(X)}|$  is much smaller.

- Thus if the system contains  $N$  noninteracting particles in a volume  $|\Lambda|$  then the ratio of  $|\Gamma_{M_{eq}}|$ , for the macrostate  $M_{eq}$  in which there are  $(\frac{1}{2} \pm 10^{-10})N$  particles in the left half of the box to  $|\Gamma_M|$ , for a macrostate  $M$  in which all the particles are in the left half is of order  $2^N$ .

- A system is then in macroscopic thermal equilibrium (MATE) iff  $X \in \Gamma_{Meq}$ .
- The fact that  $|\Gamma_{Meq}| \sim |\Gamma_E|$  justifies the use of the microcanonical ensemble to compute those properties of an equilibrium system which are represented by functions  $f(X)$  which have small fluctuations, i.e.

$$\langle f(X) \rangle \sim N, \quad \frac{\langle f^2(X) \rangle - \langle f(X) \rangle^2}{N^2} \sim \frac{1}{N}.$$

- These include all functions describing the thermodynamic properties of an equilibrium system.

# Nonequilibrium States

- Thus, most microstates, w.r.t. the uniform measure on  $\Gamma_E$ , of a macroscopic system correspond to the system being in equilibrium.
- A similar statement is true for most wave functions, in fact for most energy eigenstates, with respect to a uniform measure on the unit sphere in the shell of the Hilbert space  $\mathcal{H}_E$ .
- Fortunately there are also microstates which correspond to macroscopic systems which are out of equilibrium (or we would not be here).
- Given an  $X(t_0)$  in such a  $\Gamma_M$ ,  $M \neq M_{eq}$ , at an “initial” time  $t_0$ , we would like to know how the properties of a macroscopic system, isolated for  $t > t_0$ , change with time.
- There is also a great disparity between the sizes of the different  $\Gamma_M$ 's – the “closer”  $M$  is to  $M_{eq}$ , the larger  $|\Gamma_M|$ .

## Approach to Equilibrium

- Boltzmann (also Maxwell, Kelvin, ...) argued that given this disparity in the sizes of the  $\Gamma_M$  corresponding to the various macrostates, the evolution of a “typical” microstate  $X$ , specified to be at  $t = t_0$  in the phase space region  $\Gamma_M$ , will be such that  $|\Gamma_{M(X(t))}|$  will not decrease (on a macroscopic scale) for  $t > t_0$ .
- Typical here means that for any  $\Gamma_M$ , the relative volume of the set of microstates  $X$  in  $\Gamma_M$  for which this is false during some time period  $\tau$  during which the macrostate undergoes a macroscopically noticeable change, but not longer than the age of the universe, goes to zero exponentially in the number of atoms in the system.
- This explains and describes the evolution towards equilibrium of macroscopic systems which start in the macrostate  $\Gamma_M$ ,  $M \neq M_{eq}$ , and are kept (effectively) isolated afterwards.

# Boltzmann's Entropy

- To make a connection with the Second Law, Boltzmann defined the (Boltzmann) entropy of a macroscopic system in a microstate  $X$  as

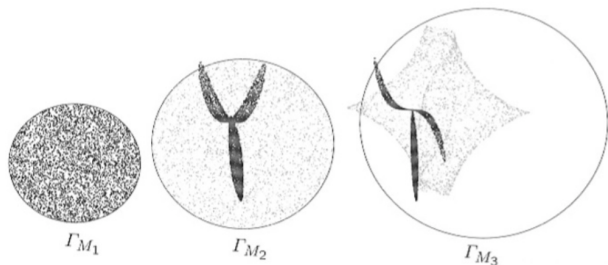
$$S_B(X) = \log |\Gamma_{M(X)}| = S_B(M). \quad (2)$$

- Thus calling  $S(E) = \log |\Gamma_E| \sim \log |\Gamma_{M_{eq}}|$ , Boltzmann showed that this definition agrees with the Clausius, i.e., thermodynamic entropy of a gas.

- The above heuristic argument, based on relative phase space volume, is the correct explanation for the behavior observed in actual macroscopic systems. It is, however, very far from a mathematical theorem and contains no quantitative information about time scales.

# Lyapunov Function for Isolated System

- We can say more mathematically if the time evolution of the macrostate  $M$ , given by  $M(X(t)) = M_t$ , effectively satisfies an autonomous deterministic equation, such as the Navier-Stokes equation or the heat equation.
- Such an equation means that if  $M_{t_1} \rightarrow M_{t_2}$ ,  $t_2 > t_1$ , then the microscopic dynamics  $T_t$  carries  $\Gamma_{M_{t_1}}$  inside  $\Gamma_{M_{t_2}}$ , i.e.  $T_{t_2-t_1}\Gamma_{M_{t_1}} \subset \Gamma_{M_{t_2}}$  and  $T_{t_3-t_2}\Gamma_{M_{t_2}} \subset \Gamma_{M_{t_3}}$  with negligible error.



# Lyapunov Function for Isolated System

- The fact that phase space volume is conserved by the Hamiltonian time evolution implies that  $|\Gamma_{M_{t_1}}| \leq |\Gamma_{M_{t_2}}|$  and thus that  $S_B(M_{t_2}) \geq S_B(M_{t_1})$  for  $t_2 \geq t_1$ . Boltzmann's argument then becomes rigorous.
- What is crucial here is that the phase points in the region in  $\Gamma_2$  coming from  $\Gamma_1$  behave, forward in time, as if they were typical of  $\Gamma_2$ . They are, however, very atypical backwards in time: if we reverse all the velocities in  $\Gamma_2$ , then at a later time most of the points initially in  $\Gamma_1$  will be in a smaller  $\Gamma_M$  region than  $\Gamma_2$ . It is here where the crucial time asymmetry, due to initial conditions, comes in.

## Going Beyond LTE: Dilute Gases

- Following Boltzmann, we refine the thermodynamic  $M$  used for systems in LTE by noting that the microstate  $X = \{\mathbf{r}_i, \mathbf{v}_i\}$ ,  $i = 1, \dots, N$ , can be considered as a set of  $N$  points in six dimensional  $\mu$ -space. We then divide up this  $\mu$ -space space into  $\tilde{J}$  cells  $\tilde{\Delta}_\alpha$ , centered on  $(\mathbf{r}_\alpha, \mathbf{v}_\alpha)$ , of volume  $|\tilde{\Delta}_\alpha|$ . A macrostate  $\tilde{M}$  is then specified by the (coarse grained) number of particles in each  $\tilde{\Delta}_\alpha$ ,

$$\tilde{M} = \{N_\alpha\}, \quad \alpha = 1, \dots, \tilde{J} \ll N.$$

- For dilute gases one can *neglect*, for typical configurations, the existence of interactions between the particles. The coarse grained energy of the system in the state  $\tilde{M}$  is given by

$$\frac{1}{2}m \sum_{\alpha} N_{\alpha} \mathbf{v}_{\alpha}^2 = E$$

$$\sum N_{\alpha} = N$$

- The phase space volume associated with such an  $\tilde{M}$  is then readily computed to be

$$|\Gamma_{\tilde{M}}| = \prod_{\alpha} (N_{\alpha}!)^{-1} |\tilde{\Delta}_{\alpha}|^{N_{\alpha}}$$

- Stirling's formula gives

$$S_B(\tilde{M}) \sim -k \left\{ \sum_{\alpha} \left( \frac{N_{\alpha}}{|\tilde{\Delta}_{\alpha}|} \log \frac{N_{\alpha}}{|\tilde{\Delta}_{\alpha}|} \right) |\tilde{\Delta}_{\alpha}| - N \right\}.$$

- Using  $\tilde{M}$  we can associate with a typical  $X$  a coarse grained density  $f_X \sim N_{\alpha}/|\tilde{\Delta}_{\alpha}|$  in  $\mu$ -space, i.e. such that  $N_{\alpha} = \int_{\tilde{\Delta}_{\alpha}} d\mathbf{x} d\mathbf{v} f_X(\mathbf{x}, \mathbf{v})$ .

- The Boltzmann entropy is then given, up to constants, by

$$S_B(X) = S_{\text{gas}}(f) = -k \int_V d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{v} f(\mathbf{x}, \mathbf{v}) \log f(\mathbf{x}, \mathbf{v})$$

- The maximum of  $S_{\text{gas}}(f)$  over all  $f$  which satisfy the conditions,

$$\int_V d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{v} f(\mathbf{x}, \mathbf{v}) = N$$

$$\int_V d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{v} \frac{1}{2} m \mathbf{v}^2 f(\mathbf{x}, \mathbf{v}) = E$$

is given by the Maxwell distribution

$$f_{\text{eq}} = \frac{N}{V} (2\pi kT/m)^{-3/2} \exp[-m\mathbf{v}^2/2kT]$$

where  $kT = 2/3(E/N)$ .

- In this case

$$S_{\text{gas}}(f_{\text{eq}}) = S(E, N, V) = Nk \left[ \frac{3}{2} \log T - \log \frac{N}{V} + \text{Const.} \right]$$

- When  $f \neq f_{eq}$  then  $f$  and consequently  $S_{\text{gas}}(f)$  will change in time.
- The microscopic version of the second law, now says that *typical*  $X \in \Gamma_{\tilde{M}}$  at the initial time  $t = 0$ , will have an  $\tilde{M}_t = \tilde{M}(X_t)$  with the property that  $S_B(\tilde{M}(X_t)) \geq S_B(\tilde{M}(X_{t'}))$ , for  $t \geq t'$ .
- This means that  $f_{X_t}(\mathbf{x}, \mathbf{v}) = f_t(\mathbf{x}, \mathbf{v})$  has to be such that  $S_{\text{gas}}(f_t) \geq S_{\text{gas}}(f_{t'})$ , for  $t \geq t'$ .
- This is exactly what happens for a dilute gas described by the Boltzmann equation.

$$\frac{d}{dt} S_{\text{gas}}(f_t) \geq 0, \quad \text{Boltzmann's } \mathcal{H}\text{-theorem}$$

As put by Boltzmann: “In one respect we have even generalized the entropy principle here, in that we have been able to define the entropy in a gas that is not in a stationary state” .

## Remark

- It is important to distinguish between the empirical smooth density  $f_{X_t}(\mathbf{x}, \mathbf{v})$  and another object with the same name, the marginal one-particle (probability) distribution  $F_1(\mathbf{x}, \mathbf{v}, t)$  obtained from an  $N$ -particle ensemble density evolving according to the Liouville equation.

## Remark cont'd

- An instructive example is a macroscopic system of  $N$  noninteracting point particles, moving among a periodic array of scatterers in a macroscopic volume  $V$ .
- Starting with a nonuniform initial density  $f_{X_0}(\mathbf{x}, \mathbf{v})$  the time evolved  $f_{X_t}(\mathbf{x}, \mathbf{v})$  will approach an  $f$  which depends only on  $|\mathbf{v}|$  and which has a larger  $S_{\text{gas}}(f)$ , while  $\int \int F_1 \log F_1 d\mathbf{x}d\mathbf{v}$  remains constant in time.
- Here the obvious evolution equation for  $f_{X_t}$ , namely the one-particle Liouville equation, in fact does not describe the evolution of  $f_{X_t}$  for times after which  $F_1(\mathbf{x}, \mathbf{v}, t)$  has developed structure on the microscopic scale.
- This distinction carries over to general systems.

# Boltzmann vs. Gibbs Entropies

- Given an ensemble (probability) density  $\mu(X)$ , the Gibbs-Shannon entropy is given by

$$S_G(\mu) \equiv -k \int_{\Gamma} \mu \log \mu dX. \quad (3)$$

- Clearly if  $\mu = \tilde{\mu}_M$ ,

$$\tilde{\mu}_M = \begin{cases} |\Gamma_M|^{-1}, & \text{if } X \in \Gamma_M; \\ 0, & \text{otherwise} \end{cases} \quad (4)$$

then

$$S_G(\mu_M) = k \log |\Gamma_M| = S_B(M). \quad (5)$$

- Unlike  $S_G(\mu)$ , which does not change in time for isolated systems and therefore is “useless” for isolated systems not in equilibrium,  $S_B(M(X))$  captures the essence of typical macroscopic behavior.
- The situation may be different for systems in contact with thermal reservoirs.

# Model of a system in contact with thermal reservoirs

- In my thesis work with Peter Bergman we studied the time evolution and stationary states of a system evolving under the combined action of its own Hamiltonian  $H$  and that of  $n$  infinite thermal reservoirs at different temperatures (and chemical potentials).
- These reservoirs were thought of as acting at the boundaries of the system and to simplify matters we idealized the interaction with the reservoirs as being of the collision type so only kinetic energies are exchanged. When such a collision occurs the phase point of the system  $X \in \Gamma$  jumps to  $X' \in \Gamma$ , while the reservoir particle goes off to infinity, never to be seen again.

# Model of a system in contact with thermal reservoirs

- The system thus sees an ever fresh stream of reservoir particles with a Maxwellian distribution, at the temperature  $T_\alpha = \beta_\alpha^{-1}$  of that reservoir,  $\alpha = 1, \dots, n$ .
- The time evolution of the system will thus be given by a continuous time Markov process.
- This is obviously an idealization which, however, should be valid in many cases for relevant time scales.

# Model of a system in contact with thermal reservoirs

- Letting  $K_\alpha(X, X')dX$  be the transition rate from  $X'$  to  $dX$ , yields the following stochastic Liouville master equation for the probability distribution, aka ensemble density,  $\mu(X, t)$ ,

$$\begin{aligned} \frac{\partial \mu(X, t)}{\partial t} + \{\mu, H\} &= \\ &= \sum_{\alpha=1}^n \int [K_\alpha(X, X')\mu(X', t) - K_\alpha(X', X)\mu(X, t)] dX', \end{aligned} \quad (6)$$

where  $H$  is the Hamiltonian of the system and  $\{\mu, H\}$  is the usual Poisson bracket describing the deterministic Hamiltonian evolution of the isolated system.

# Model of a system in contact with thermal reservoirs

- Using the time reversibility of the collision dynamics yields a condition for each  $\alpha$ ,

$$K_\alpha(X, X') = e^{\beta_\alpha H(X')} L_\alpha(X, X') \quad (7)$$

with

$$L_\alpha(X, X') = L_\alpha(\bar{X}', \bar{X}), \quad (8)$$

where  $\bar{X} = \mathcal{R}(X)$  corresponds to reversal of the velocity coordinates.

- Some further simplifications give  $L_\alpha(\bar{X}', \bar{X}) = L_\alpha(X', X)$ , so that  $L_\alpha(X, X') = L_\alpha(X', X)$ , corresponding to “detailed balance” for each reservoir.

# Model of a system in contact with thermal reservoirs

- We proved, under quite general conditions on the  $L_\alpha(X, X')$  that, as  $t \rightarrow \infty$ , the system will approach a stationary state

$$\lim_{t \rightarrow \infty} \mu(X, t) = \mu_s(X). \quad (9)$$

- This state is unique and is absolutely continuous with respect to Liouville measure. When the  $\beta_\alpha$  are all the same,  $\beta_\alpha = \beta$ , then clearly

$$\mu_s(X) = \mu_\beta(X) \equiv Z^{-1} \exp[-\beta H(X)] \quad (10)$$

is the unique stationary state.

- If the temperatures  $\beta_\alpha^{-1}$  are different  $\mu_s$  will be a non-equilibrium stationary state (NESS), for which the dynamics do not satisfy detailed balance. We further proved that this NESS will satisfy the Onsager reciprocal relations for all  $\beta_\alpha$  close to some  $\bar{\beta}$ , as well as a generalized Kubo relation in the presence of an external field.

# Model of a system in contact with thermal reservoirs

- When the system is in contact with stochastic reservoirs,  $S_G(\mu)$  will change with time,

$$\frac{d}{dt} S_G(\mu) = \sigma_G(t) + \sum_{\alpha=1}^n J_\alpha(t)/T_\alpha. \quad (11)$$

- The second contribution contains  $J_\alpha$ , which is the average energy flux *from* the  $\alpha$ th reservoir into the system, that is

$$J_\alpha(t) = \int \mu(X, t) \int K_\alpha(X', X) [H(X') - H(X)] dX' dX. \quad (12)$$

# Model of a system in contact with thermal reservoirs

- These fluxes satisfy the energy balance relation

$$\frac{d}{dt} \int H(X) \mu(X, t) dX = \sum_{\alpha=1}^n J_{\alpha}(t). \quad (13)$$

- The first contribution is,

$$\begin{aligned} \sigma_G(t) = & \frac{1}{2} \sum_{\alpha=1}^n \int \int L_{\alpha}(X, X') [\nu_{\alpha}(X, t) - \nu_{\alpha}(X', t)] \times \\ & \times \log \left[ \frac{\nu_{\alpha}(X, t)}{\nu_{\alpha}(X', t)} \right] dX dX' \geq 0, \end{aligned} \quad (14)$$

where

$$\nu_{\alpha}(X, t) = \mu(X, t) \exp[\beta_{\alpha} H(X)]. \quad (15)$$

- Equation (11) can be rewritten in the suggestive form

$$\sigma_G(\mu) = \frac{\bar{d}S_{\text{res}}}{dt} + \frac{dS_G}{dt} \geq 0 \quad (16)$$

where we have written  $\bar{d}S_{\text{res}}/dt = \sum_{\alpha} \bar{d}S_{\alpha}/dt$  and

$$\frac{\bar{d}S_{\alpha}}{dt} = -J_{\alpha}/T_{\alpha} \quad (17)$$

for the rate of change of the entropy of the  $\alpha$ th reservoir caused by the energy (heat) flow *into* that reservoir.

- *This expression is reminiscent of the second law, but note that all the entropy production  $\sigma_G$  is caused by the stochastic interactions which will generally occur for a macroscopic system at its surface, rather than by the dissipative flows, due the chaotic microscopic dynamics, in the bulk of the system, as it should be from a nonequilibrium thermodynamic point of view.*

## Boltzmann entropy, thermal reservoirs

To see this bulk entropy production, we now consider the behavior of the hydrodynamic or Boltzmann entropy of the system, assumed to be “chaotic”, in contact with several reservoirs. After some local relaxation time, it will be in a local equilibrium state with a temperature profile  $T(\vec{r}, t)$ , where  $\vec{r}$  denotes different spatial points of the system. The thermodynamic (hydrodynamic) entropy, which is also the Boltzmann entropy, is given, as noted earlier, by an integral over the volume  $V$  of the system

$$S_B(t) = \int_V s_{\text{eq}}(T(\vec{r}, t)) d\vec{r}. \quad (18)$$

with  $s_{\text{eq}}(T) = \lim[S(T, N, V)/V]$

- Starting then with the general equation for the entropy density of a system in LTE

$$\frac{\partial s(\vec{r}, t)}{\partial t} = -\frac{\text{div } j(\vec{r}, t)}{T(\vec{r}, t)} = -\text{div } (j/T) + j \cdot \nabla \left( \frac{1}{T} \right), \quad (19)$$

where  $j(\vec{r}, t)$  is the energy flux vector, we get for a system in contact with thermal baths.

$$\begin{aligned} \frac{dS_B}{dt} &= \int_Q \frac{j(q, t)}{T(q)} dq + \int_V j(r, t) \cdot \nabla \left( \frac{1}{T(r)} \right) d\vec{r} \\ &= -\frac{dS_r}{dt} + \sigma_B, \quad \text{with } \sigma_B \geq 0 \end{aligned} \quad (20)$$

where  $Q$  is the surface of  $V$ , parts of which are in contact with different reservoirs at temperatures  $T(q)$ , with  $q \in Q$ . The first term can be identified with the entropy production in the reservoirs, while the second term corresponds to the Boltzmann entropy production,

$$\sigma_B(t) = \int_V j(\vec{r}, t) \cdot \nabla \left( \frac{1}{T(\vec{r}, t)} \right) d\vec{r} \quad . \quad (21)$$

- In contrast with  $\sigma_G(\mu)$ ,  $\sigma_B$  is a positive entropy production in the bulk of the system, due to local “dissipation” rather than something that happens just at the place where the system interacts with some reservoir given by  $\sigma_G$  in Eq. 14.

- We expect however that if the system is macroscopic and chaotic, i.e. it satisfies Fourier's law locally, then the energy density profile in the stationary state computed as an average over  $\mu_s$  will be that corresponding to LTE.
- The entropy production  $\sigma_G(\mu_s)$  occurring at the surface only will then be equal to that given by  $\sigma_B$

$$\sigma_G(\mu_s) = \sigma_B = - \sum_{\alpha} J_{\alpha} / T_{\alpha} \quad , \quad (22)$$

since  $dS_G(\mu_s)/dt = 0$ .

- This raises the question of whether  $S_G(\mu_s) = S_B$  in the stationary state as given in (18).
- Put another way, to what extent is the stationary measure  $\mu_s$  for a “chaotic” system, i.e. one satisfying Fourier’s law, correspond to a LTE state, when the only stochasticity is the one at the surface.
- This can be proven to be the case when there are also bulk stochastic interactions which conserve energy, either fully or just on the average (Olla, et al.).
- This may however not be the case when the bulk dynamics is Hamiltonian which does not change  $S_G$ . In fact this is not true for deterministic dissipative reservoirs corresponding to Gaussian thermostats at the surface.

# Small systems in contact with a thermal reservoir

- What about  $S_G(\mu)$  for small systems in contact with a thermal bath with some specified  $\mu$ ?
- The paradigm of such a system is a Brownian particle immersed in an equilibrium fluid at temperature  $T$ .
- The only relevant degree of freedom for such a (spherical) particle is the location of its center of mass.

# Small systems in contact with a thermal reservoir

- For a sufficiently idealized fluid and a Brownian particle, a Fokker-Planck equation for  $\mu(\vec{r}, \vec{v}, t)$  is

$$\frac{\partial \mu}{\partial t} + \vec{v} \cdot \frac{\partial \mu}{\partial \vec{r}} - \frac{\partial U}{\partial \vec{r}} \cdot \frac{\partial \mu}{\partial \vec{v}} = \xi \frac{\partial}{\partial \vec{v}} \cdot \left[ \mu_{\beta} \frac{\partial}{\partial \vec{v}} (\mu / \mu_{\beta}) \right] \quad , \quad (23)$$

where  $\mu_{\beta} = Z^{-1} \exp \left\{ -\beta \left[ \frac{1}{2} |\vec{v}|^2 + U(\vec{r}) \right] \right\}$ .

- The particle distribution then evolves towards its stationary value  $\mu_{\beta}$  (exponentially) on a time scale which depends on  $\xi$ .

# Small systems in contact with a thermal reservoir

- For the Fokker-Planck equation 23

$$\sigma_G = \xi \int \mu(\vec{r}, \vec{v}, t) \left| \frac{\partial}{\partial \vec{v}} \log \nu \right|^2 d\vec{r} d\vec{v} = \frac{dS_G}{dt} - J/T \geq 0 \quad , \quad (24)$$

where  $\nu = \mu/\mu_\beta$  as in Eq. 15 and  $J$  is the average energy flux from the fluid to the Brownian particle  $J = \frac{d}{dt} \int \mu \frac{1}{2} |\vec{v}|^2 d\vec{r} d\vec{v}$ .

## Small systems in contact with a thermal reservoir

- Equations 23 and 24 and their analogues play a central role in “stochastic thermodynamics” where  $S_G(\mu)$  is generically taken for granted to represent a thermodynamic entropy and thus 24 is considered to be an expression of the second law.
- There are in fact, as already noted, recent experiments [ ] which give some support to this interpretation.
- The question therefore naturally arises of why this should be true for small systems in contact with thermal reservoirs when, as argued above, this is not the case for isolated systems and may not be true for systems in contact with reservoirs at their surfaces.

# The Brownian gas

- To justify this, consider a dilute gas of  $N$  such Brownian particles,  $N \gg 1$ , and call it a Brownian gas. The gas is so dilute that interactions between the Brownian particles are negligible. This Brownian gas is a macroscopic system in contact with a thermal reservoir not just at its boundaries, but “everywhere”.

# The Brownian gas

- The “meso” macro state of the Brownian gas is given, as for an isolated gas discussed earlier, by the smoothed empirical density  $f(\vec{r}, \vec{v})d\vec{r}d\vec{v}$ .
- This corresponds to a region  $\Gamma_f$ , in  $\Gamma$ , the log of whose Liouville volume, denoted  $|\Gamma_f|$ , is given, up to constants, by the same expression Boltzmann obtained for an isolated dilute gas

$$\log |\Gamma_f| = - \int f(\vec{r}, \vec{v}) \log f(\vec{r}, \vec{v}) d\vec{r}d\vec{v}. \quad (25)$$

- The Boltzmann entropy of this meso state is given by

$$S_B(\{f\}) = \log |\Gamma_f| = - \int f \log f d\vec{r}d\vec{v} + \text{const.} \quad (26)$$

# The Brownian gas

- Identifying the observed  $\mu$  for a single B-particle with  $f$  (normalized), the right hand side of Eq. (26) coincides, up to a constant term, with  $NS_G(\mu)$ .
- This is so even though the physical interpretations of  $NS_G(\mu)$  and  $S_B(f)$  are quite different.

# The Brownian gas

- The entropy production of a Brownian gas plus fluid is given by

$$\sigma_B = -\frac{d}{dt} \int f \log f d\vec{r}d\vec{v} - J_N/T \geq 0 \quad , \quad (27)$$

where  $J_N$  is the flux of energy from the fluid to the Brownian gas.

- Thus  $-J_N/T$  is the rate of entropy change of the fluid at temperature  $T$ .
- The right side of equation 27 is just  $N$  times the right hand side of equation 24 if one identifies  $J_N = NJ$ . Since we have idealized the fluid as an infinite reservoir, its entropy is formally infinite, but its rate of change is finite.

# The Brownian gas

- The important observation now is that unlike the case of an isolated gas, where some interaction between the particles is essential to make the system satisfy the second law (rather than behaving like an ideal gas), the Brownian gas gets thermalized via its interaction with the fluid.
- *Hence the behavior of a single Brownian particle averaged over many trials will be the same as that of a Brownian gas. It is therefore meaningful to consider the Gibbs-Shannon entropy of a single Brownian particle as having a thermodynamic meaning, i.e. being equal to that of a Brownian gas divided by the number of particles.*
- This should be true both when the Brownian gas is in global equilibrium, or in a meso (macro) state described by  $f$ , which can be more or less arbitrary.

- The above considerations will hold also in the case when the Brownian particle is acted on by an external potential  $U(\vec{r}, t)$ .
- The Brownian gas will act, and thus also repeated experiments on a single Brownian particle, like a macroscopic system, subject to the second law.
- In particular when  $U(\vec{r}, t)$  varies sufficiently slowly in time compared to the time it takes the Brownian particle to relax to equilibrium with the instantaneous value of  $U(\vec{r}, t)$ , then the entropy will change adiabatically and the right side of (24) will be an equality. This is what is observed in the experiments of Bechhoefer et al which I will discuss next.

# Experiments on a Brownian particle

An idealized simplified version of the experiment is as follows:

- At  $t = 0$  the particle is in equilibrium with the fluid at an external potential  $U_0(\vec{r})$ .
- At  $t = 0$ ,  $U_0(\vec{r})$  is changed to  $U_1(\vec{r})$  without any work being done, e.g. one suddenly removes a wall (infinite potential) confining the particle to part of the fluid.
- One then waits until time  $t_1$  for the particle to come to equilibrium with the fluid at the new potential  $U_1(\vec{r})$ , e.g. no confining potential.
- One then changes  $U_1$  to  $U_0$  over a time interval  $\tau$ . During this time one does work  $W$  on the particle.

# Experiments on a Brownian particle

- When the time variation of  $U(\vec{r}, t)$  during  $\tau$  is very slow compared to the relaxation time of the particle to its equilibrium distribution, then the macro (meso) state of the Brownian gas is given by

$$f(\vec{r}, \vec{v}, t) = N\mu_\beta,$$

$$\mu_\beta(\vec{r}, \vec{v}, t) = \frac{1}{Z(t)} \exp\left(-\beta \left[\frac{|\vec{v}|^2}{2} + U(\vec{r}, t)\right]\right), \quad (28)$$

with  $U(\vec{r}, 0) = U(\vec{r}, t_1 + \tau) = U_0(\vec{r})$ .

# Experiments on a Brownian particle

- Using now standard thermodynamics for quasi-static changes permits relating the work done,  $W(\tau)$ , on the B-gas during this phase to the change of its free energy, given by  $-T \log Z$ , during the period  $\tau$ . This will be the same for repeated experiments on a B-particle.

$$\begin{aligned}\langle W(\tau) \rangle &= - \int_{t_1}^{t_1+\tau} \dot{\vec{r}} \cdot \frac{\partial U(\vec{r}, t)}{\partial t} \mu_\beta(\vec{r}, \vec{v}, t) d\vec{r} d\vec{v} \\ &= \int_{t_1}^{t_1+\tau} \frac{\partial}{\partial t} [U(\vec{r}, t)] \mu_\beta(\vec{r}, \vec{v}, t) d\vec{r} d\vec{v} = T \log[Z(t_1)/Z(t_1 + \tau)] \\ &= E(t_1 + \tau) - E(t_1) - T[S_G(t_1 + \tau) - S_G(t_1)].\end{aligned}\tag{29}$$

# Experiments on a Brownian particle

- In the actual experiment the only relevant energy of the B-particle was kinetic energy, so  $E(t_1) = E(0) = E(t_1 + \tau)$ .
- Furthermore,  $W(\tau)$  was shown experimentally, and can be argued analytically, to have very little variance for large  $\tau$ .
- Hence measuring  $W(\tau)$  in a single experiment lets you measure  $S_G(\mu_\beta(t_1)) - S_G(\mu_\beta(t_1 + \tau))$  for different external potentials  $U(\vec{r}, t)$ , e.g. for different confining volumes of  $U_0(\vec{r})$ .

# Experiments on a Brownian particle

- When  $\tau$  is not so large then there will be extra entropy production in the Brownian gas during this period.
- $\langle W(\tau) \rangle$  in (29) should be and was measured to be greater than the right hand side.
- In the analysis of the experiment and in stochastic thermodynamics one goes beyond the simple equality or inequality of (29).
- One actually computes the distribution of  $W(\tau)$ . I shall not go into that here.

Let me turn now to quantum systems: large and small

- I will take, as indicated before, the microstate of such a system to be its wave function  $\psi \in \mathcal{H}_E$ , where  $\mathcal{H}_E$  is a shell of thickness  $\Delta E$ .
- The question then is which  $\psi$  corresponds to the system being in macroscopic thermal equilibrium (MATE).

- Following von Neumann, we take the macro-observables  $\hat{M}_j$  to commute with each other. We assume that this can be achieved by suitably “rounding off”, i.e. coarse-graining, the operators representing the macro-observables.
- Taking  $\mathcal{H}_E$  to be an eigenspace of a “macro energy” operator, and thus to commute with the other macro-observables, all  $\hat{M}_j$  can be regarded as operators on  $\mathcal{H}_E$ .
- Their joint spectral decomposition defines an orthogonal decomposition

$$\mathcal{H}_E = \bigoplus_{\nu} \mathcal{H}_{\nu}, \quad (30)$$

The subspaces  $\mathcal{H}_{\nu}$  (“macro spaces”), the joint eigenspaces of the macro-observables, correspond to the different macro states and have very high dimension,  $d_{\nu} = \dim \mathcal{H}_{\nu} \gg 1$ , for macroscopic systems

- As in the classical case, it is generally true that one of the  $\mathcal{H}_\nu$ , denoted  $\mathcal{H}_{eq}$ , has most of the dimensions of  $\mathcal{H}_E$ , i.e.,

$$\frac{\dim \mathcal{H}_{eq}}{\dim \mathcal{H}_E} = 1 - \varepsilon \quad (31)$$

with  $\varepsilon \ll 1$ .

- The Boltzmann entropy  $S_B(\{\psi\})$  of a system whose  $\psi$  is in (or close to)  $\mathcal{H}_\nu$ ,  $\langle \psi | P_\nu | \psi \rangle$ , is  $\log d_\nu$ .
- Most everything we said about isolated classical macroscopic systems then also holds for quantum systems.
- However, unlike classical systems where any subsystem of a system in a pure state is also in a pure state, the subsystem of quantum systems with a wave function  $\psi$  will be described by a density matrix  $\hat{\rho}_S$ .

- We now define a system with wave function  $\psi$  to be in microscopic thermal equilibrium (MITE) if, for any not-too-large subsystem  $S$ , the reduced density matrix of  $S$  is close to the thermal equilibrium density matrix of  $S$ ,

$$\hat{\rho}_S^\psi \approx \hat{\rho}_S^{mc}, \quad (32)$$

where

$$\hat{\rho}_S^\psi = \text{tr}_{S^c} |\psi\rangle\langle\psi| \quad (33)$$

is the reduced density matrix of  $S$  obtained by tracing out the complement  $S^c$  of  $S$ , and

$$\hat{\rho}_S^{mc} = \text{tr}_{S^c} \hat{\rho}^{mc} \quad (34)$$

- It turns out that for macroscopic systems MITE implies MATE.
- However, it is possible for even very small quantum systems (such as 7 spins whose Hilbert space has dimension 128) to be in MITE.
- That is, for a system in an energy eigenstate, the reduced density matrices of a subsystem smaller than half of the full system (say a single or pair of spins) will be close to that obtained from a micro-canonical density matrix of the whole system, giving equal weight to all energy eigenstates in a shell around  $E$ , the energy of the pure state.
- This has been found both numerically and experimentally.

- When the initial wave function, pure state, for such a system is chosen "randomly", having mean energy  $E$  one finds an approach to a MITE state (on a time scale short compared to that of the quasi-periodic recurrence time) with oscillations of amplitude of the order of the reciprocal of the square root of the dimension of the relevant Hilbert space.
- This is consistent with the "eigenstate thermalization hypothesis" (ETH) for macroscopic "chaotic" quantum systems extended to be approximately valid for small systems.
- There are, of course, no macro variables for such small systems and this raises the question about the possible differences between classical and quantum mechanics in how large a system has to be in order to have thermodynamics, e.g. the second law, applicable.

- We should remember here that the effective number of degrees of freedom for a quantum system may be larger than for a classical system due to the possibility of linear superposition of wave functions in the Hilbert space whose dimension is exponential in the number of degrees of freedom.

## Example:

- Consider a system of  $N$  particles in a box  $V$ . At  $t = 0$  all the particles are in  $J$ , the left half of  $V$ ,  $n(0) = N$ .
- We consider now the time evolution of  $n(t)$ , the number of particles in  $J$  at time  $t > 0$ . We expect this to show "irreversible" behavior for large  $N$ , i.e.  $n(t)$  will decrease, more or less, monotonically until  $n(t)/N$  is close to  $1/2$ .
- Think, for the sake of concreteness, of the particles as hard balls, with a total energy  $E$  confined by a wall around  $J$  which is removed at  $t = 0$ .

- The meaning of  $n(t)$  is clear for a classical system evolving under Hamiltonian dynamics of  $X(t)$ , a point in the phase space of the system,  $n(t) = n(X(t))$ . Then if  $X(0)$  is "typical" of the micro canonical ensemble in  $J$  we would come up with some estimate for how large  $N$  has to be in order to "see" irreversible behavior, which will not be too small.
- If on the other hand we consider the time evolution of the initial ensemble then we will presumably see irreversible behavior, e.g.,  $\langle n(t) \rangle$  will be monotone, even for very few particles. We would have to look at the variance of  $n(t)$  to see the size effects. (This is the ensemblist point of view which we reject for classical systems.)

- In quantum mechanics we would consider the initial micro state as represented by a wave function  $\psi(0)$  confined to  $J$ , which is picked at "random" from the micro canonical ensemble.
- The meaning of  $n(t)$  then depends on whether one uses Bohmian (B) or Copenhagen (C) or .....interpretations of quantum mechanics.
- In B the meaning of  $n(t)$  is clear and its dependence on  $N$  should be similar to the classical case. (How similar?).
- On the other hand the behavior of  $|\psi(t)|^2$  should be similar to that of the ensemble evolution in the classical case (How similar?)
- In the C interpretation  $n(t)$  is an operator and the only thing we can look at is the evolution of  $\psi$ , so one would have to say that  $N$  can be small and look at the  $N$  dependence of the variance of  $n(t)$ . This would be the same as for  $B$  and presumably similar to that of the classical ensemble.

- One should also mention here that in the classical limit of quantum mechanics the energy eigenfunctions (absolute value squared) go into microcanonical densities.
- One may therefore consider choosing a minimal dispersive coherent wavefunction as the analogue of a random phase point  $X$  classically.
- There is also in quantum mechanics the problem of quasi periodicity of  $\psi$  or the density matrix which does not exist for the classical ensemble evolution of a chaotic (mixing) system.