

Energy - from order to disorder

What happens with the ordered system (zero entropy), when it at constant temperature gradually evolves to the equilibrium (some finite entropy). Does it emits the energy ? Where does the delta energy goes ?

That's an *excellent* and very deep question — and you're now touching on the **thermodynamic meaning of entropy increase, energy dissipation, and the arrow of time**.

Let's go step by step — this is one of those moments where everything about thermodynamics, statistical mechanics, and even information theory comes together beautifully.

♦ 1. The setup

You start with an **ordered system** (low entropy, $S_1 = 0$, all spins aligned).

It is in contact with a **thermal reservoir** at constant temperature T .

Then you let it **relax toward equilibrium** — meaning it gradually becomes disordered, increasing its entropy to $S_2 > 0$.

The question:

What happens energetically during this relaxation?
Does it emit energy, and where does that energy go?

♦ 2. The key relation: $\Delta F = \Delta U - T\Delta S$

At constant T ,

$$dF = dU - T dS.$$

In equilibrium thermodynamics:

- The **Helmholtz free energy** F always decreases spontaneously (it's the Lyapunov function for systems at constant T and V):



$$\Delta F < 0.$$

- This decrease in F corresponds to *useful work that can no longer be extracted*—the system relaxes toward equilibrium.

♦ 3. What happens to the energy

During relaxation:

- **Entropy increases:** $\Delta S > 0$,
- **Internal energy may or may not change** depending on microscopic details,
- But in all cases, **heat** Q is released to the reservoir.

From the first law:

$$\Delta U = Q + W,$$

and for a system that does no mechanical work ($W = 0$):

$$Q = \Delta U.$$

The second law (for the total system + bath):

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{bath}} \geq 0.$$

At constant T :

$$\Delta S_{\text{bath}} = -\frac{Q}{T}.$$

So:

$$\Delta S_{\text{system}} - \frac{Q}{T} \geq 0.$$

If the system's entropy increases ($\Delta S_{\text{system}} > 0$), that means $Q > 0$: **heat flows from the system to the bath.**

♦ **Therefore:**

As the ordered system becomes disordered (entropy increases), it **releases energy as heat** to the reservoir.

The amount of heat released is:

$$Q = T\Delta S,$$

because at constant T ,

$$\Delta F = \Delta U - T\Delta S = -T\Delta S \quad (\text{if } \Delta U = 0).$$

♦ **4. Where does that energy go?**

It goes into the **thermal bath** (environment).

Physically:

- Microscopic degrees of freedom (spins, vibrations, etc.) randomly fluctuate,
- The ordered state loses its constraints,
- The released energy increases the microscopic agitation of the reservoir.

So the reservoir's internal energy increases by exactly $Q = T\Delta S$, while its temperature remains (almost) constant because it's large.

♦ **5. Intuitive interpretation**

Think of it this way:

- To create order, you had to **invest** TS of energy (do work).
- When the system relaxes, that **stored ordering energy** is **released back** as heat into the environment.
- The system "uses up" its order potential and returns to thermal equilibrium.

That's why the **free energy decreases** during spontaneous relaxation:

$$\Delta F = -T\Delta S < 0.$$

♦ 6. Concrete example: ordered spins relaxing

Suppose you have N non-interacting spins at $T = 300$ K.


- Ordered state: $S_1 = 0$.
- Equilibrium random state: $S_2 = Nk \ln 2$.
- Entropy increase: $\Delta S = Nk \ln 2$.
- Energy released: $Q = T\Delta S = NkT \ln 2$.

For **1 mole** ($N = N_A$):

$$Q = N_A k T \ln 2 = RT \ln 2 \approx 1.7 \text{ kJ/mol.}$$

So, the system emits about **1.7 kJ of heat per mole** as it relaxes from a perfectly ordered to a random configuration at 300 K.

♦ 7. The big picture analogy

Concept	Meaning	
Creating order	Requires energy input $+TS$ — doing work to constrain randomness	
Relaxation (entropy increase)	Releases energy TS — system gives up its “order potential”	
Constant temperature	Means the environment absorbs or supplies heat without changing its own T	
Direction of time	Energy flow from system to bath accompanies entropy increase — defines irreversibility	

✓ Summary in one line:

When an ordered system (zero entropy) relaxes to equilibrium at constant temperature, it **emits energy** $Q = T\Delta S$ as heat to the environment — the energy that was previously “stored” in its ordered configuration.

what if the ordered system is isolated, no contact with bath, how does it relaxes to equilibrium

Excellent — this is **exactly** the right next question.

You're now asking:

If the ordered system is *isolated* (no contact with a reservoir, no external heat exchange), can it still "relax" to equilibrium — and if so, **how** and **what drives that process**?

The answer depends on what kind of system we're talking about, and it brings out a deep distinction between **thermodynamic equilibrium** and **statistical equilibrium** in isolated systems.

Let's unpack this very carefully.

♦ 1. Isolated system: no exchange of energy or matter

By definition:

$$\Delta U = Q + W = 0,$$

so $Q = 0$ (no heat exchange) and $W = 0$ (no work done by or on the surroundings).

Therefore, the **total energy** U of the system is constant.

♦ 2. Entropy in an isolated system

For an isolated system, the **Second Law** still applies:

$$\Delta S_{\text{system}} \geq 0.$$

But now, since there's no external reservoir, any entropy increase must come from **internal processes**.

That means:

The system can spontaneously evolve from a low-entropy microstate to a high-entropy one, provided energy remains constant — by redistributing energy *internally* among its degrees of freedom.

This is called **internal equilibration** or **mixing**.

♦ 3. Microscopic picture — redistribution, not exchange

Even if total energy is fixed, there are typically **many microstates** that correspond to the same energy E .

An initially ordered configuration occupies a **very special, extremely small region** of that energy surface in phase space.

Over time, if the dynamics are **ergodic or chaotic**, the system's trajectory explores the accessible phase-space region corresponding to that total energy E .

That exploration causes the **macroscopic observables** (like magnetization, spatial order, etc.) to “relax” toward their equilibrium values —

not because the system exchanges energy, but because it **redistributes** energy internally among its microscopic degrees of freedom.

♦ 4. Example: isolated spin system

Let's revisit your spin example:

- Initially all spins are aligned → minimal entropy, special microstate.
- Energy $E = -N\mu B$ if B is present (or $E = 0$ if $B = 0$).
- Isolated → total energy constant.

Now, for non-interacting spins **without an external field**, all configurations have the same energy. So, there is *no energetic barrier* preventing reorientation.

Quantum or thermal fluctuations within the system (spin-spin couplings, small perturbations, imperfections) can cause spins to flip over time, exploring other configurations with the same total energy.



Eventually, the system becomes **maximally mixed** — all spin orientations equally probable — even though the total energy never changed.

The entropy increases because the system now occupies a much larger region of phase space consistent with that same total energy.

♦ 5. Where does the "ordering energy" go?

This is the subtle but crucial point:

- In an *open* system, the energy $T\Delta S$ is *emitted as heat* to the environment.
- In an *isolated* system, that same energy change manifests as an *internal redistribution*: the macroscopic order parameter loses energy, which is transferred to microscopic motions (internal "heat").

So the *total energy remains constant*, but **the form of energy changes**:

$$E_{\text{ordered modes}} \rightarrow E_{\text{disordered internal degrees of freedom}}$$

You can think of this as the system "heating itself up" internally — macroscopic order transforms into microscopic kinetic agitation.

♦ 6. Entropy increase without energy change

This is precisely how **entropy** increases even when U is constant:

- Entropy counts the number of accessible microstates at a given energy.
- The system's dynamics "spread out" in phase space, occupying more of that constant-energy surface.
- The coarse-grained description becomes more uniform — hence, higher entropy.

Mathematically, the fine-grained Liouville entropy remains constant (because Hamiltonian flow preserves phase-space volume),

but the **coarse-grained entropy** — the one relevant for macroscopic observation — increases due to mixing.

♦ 7. Summary of both cases

System Type	Exchange?	What drives relaxation?	Where does $T\Delta S$ go?
Open (constant T)	Heat exchange with reservoir	Entropy increase + energy flow	Released as heat to bath
Isolated (constant U)	No exchange	Internal mixing / redistribution	Converted into internal microscopic agitation (disordered degrees of freedom)

♦ 8. Physical intuition

Think of a perfectly aligned row of spins, or an ordered lattice, as having “stored coherence.” When isolated, microscopic interactions (spin–spin coupling, phonons, small perturbations) gradually **scramble** that coherence.

You don’t need an external bath — just *chaotic internal dynamics*.

The order “melts” into microscopic disorder, even though total energy is conserved.

In other words:

The system loses *macroscopic order* but gains *microscopic disorder* — energy is conserved, entropy increases.

✓ Summary statement

In an isolated system, relaxation toward equilibrium occurs through *internal redistribution of energy*, not through exchange with the environment.

The ordered (low-entropy) degrees of freedom lose their coherent energy, which becomes microscopic agitation of other modes.

The total energy remains constant, but the system’s entropy increases as it explores a larger portion of phase space consistent with that energy.

