Lecture 5: 2nd and 3rd Laws of Thermodynamics

An isolated system, being initially in a non-equilibrium state, will evolve from macropartitions with lower multiplicity (lower probability, lower entropy) to macropartitions with higher multiplicity (higher probability, higher entropy). Once the system reaches the macropartition with the highest multiplicity (highest entropy), it will stay there.

2nd law: The entropy of an *isolated* system never decreases.

$$T \equiv \left(\frac{\partial S(U, V, N, \ldots)}{\partial U} \right)_{V,N}^{-1}$$

Nernst's Theorem: The entropy of a system at ***T* = 0** is a well-defined constant. For any processes that bring a system at ***T* = 0** from one equilibrium state to another, Δ ***S* = 0** .

Measuring Entropy

Even if we cannot calculate ***S***, we can still measure it:

For ***V=const*** and ***N=const*** :

$$dS = \frac{dU}{T} = \frac{\delta Q}{T} = \frac{C_V(T)\,dT}{T}$$

$$\boxed{dS = \frac{\delta Q}{T}}$$

- in L.6, we'll see that this equation holds for all ***reversible*** (quasi-static) processes (even if ***V*** is changed in the process).

This is the "thermodynamic" definition of entropy, which Clausius introduced in 1854, long before Boltzmann gave his "statistical" definition $S \equiv k_B \ln \Omega$.

$$\boxed{S(T) - S(0) = \int_0^T \frac{C_V(T')\,dT'}{T'}}$$

By heating a cup of water (200g, C_V =840 J/K) from 20^{0}C to 100^{0}C, we increase its entropy by

$$\Delta S = \int_{293}^{373} (840\ \text{J/K}) \frac{dT'}{T'} = 200\ \text{J/K}$$

At the same time, the multiplicity of the system is increased by $e^{1.5\times 10^{25}}$

From $S(N,U,V)$ - to $U(N,T,V)$

Now we can get an (energy) equation of state $U = f\,(T,V,N,...)$ for any system for which we have an explicit formula for the multiplicity (entropy)!! ***Thus, we've bridged the gap between statistical mechanics and thermodynamics!*** The recipe:

- Find $\Omega\,(U,V,N,...)$ – the most challenging step
- $S\,(U,V,N,...) = k_B \ln \Omega\,(U,V,N,...)$
- $T \equiv \left(\dfrac{\partial S(U,V,N,...)}{\partial U} \right)_{V,N}^{-1}$
- Solve for $U = f\,(T,V,N,...)$

An Einstein Solid: from *S*(*N*,*U*) to *U*(*N*,*T*) at high *T*

High temperatures:

($k_B T >> \varepsilon$, $q >> N$)

$$\Omega(N,U) = \left(e\frac{q}{N}\right)^N = \left(\frac{eU}{N\varepsilon}\right)^N$$

$$S(U,N) = N k_B \ln\left(\frac{eU}{N\varepsilon}\right) = N k_B \ln U + N k_B \ln\left(\frac{e}{N\varepsilon}\right)$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{N k_B}{U}$$

$$\boxed{U(N,T) = N k_B T}$$

- in agreement with the equipartition theorem: the total energy should be **½$k_B T$** times the number of degrees of freedom.

To compare with experiment, we can measure the heat capacity:

$$C \equiv \frac{\delta Q}{dT} = \frac{dU + PdV}{dT}$$

the heat capacity at constant volume

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}$$

$$C_V = \frac{\partial}{\partial T}\left(N k_B T\right) = N k_B$$

- in a nice agreement with experiment

An Einstein Solid: from *S*(*N*,*U*) to *U*(*N*,*T*) at low *T*

Low temperatures:

(***$k_BT \ll \varepsilon$, q*** **$\ll$N**)

$$\Omega(N,U) = \left(\frac{eN}{q}\right)^q = \left(\frac{eN\varepsilon}{U}\right)^{\frac{U}{\varepsilon}}$$

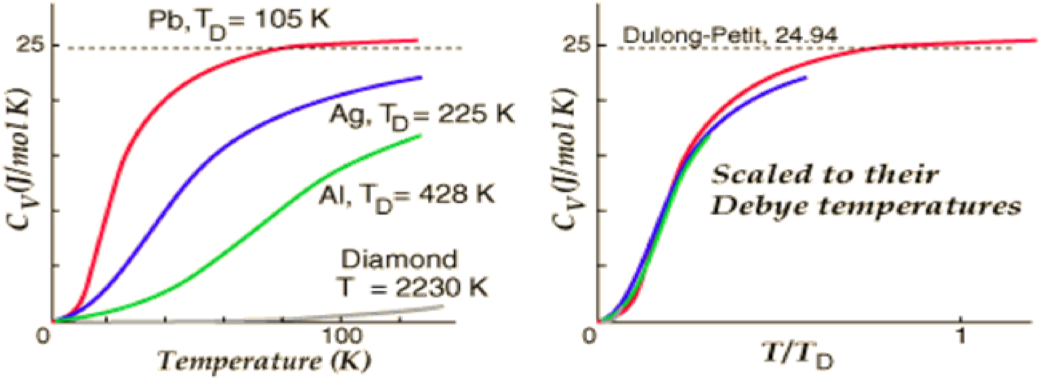
$$S(N,U) = \frac{k_BU}{\varepsilon}\ln\left(\frac{eN\varepsilon}{U}\right)$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{k_B}{\varepsilon}\ln\left(\frac{eN\varepsilon}{U}\right) - \frac{k_B}{\varepsilon} = \frac{k_B}{\varepsilon}\ln\left(\frac{N\varepsilon}{U}\right) \quad \Rightarrow \quad \boxed{U(N,\varepsilon,T) = N\,\varepsilon\, e^{-\frac{\varepsilon}{k_BT}}}$$

- as ***T*** → 0, the energy goes to zero as expected (*Pr*. 3.5).

The low-***T*** heat capacity:

(more accurate result will be obtained on the basis of the Debye model of solids)



$$C_V = \frac{\partial}{\partial T}\left(N\varepsilon\, e^{-\frac{\varepsilon}{k_BT}}\right) = N\varepsilon\; e^{-\frac{\varepsilon}{k_BT}}\left(\frac{\varepsilon}{k_BT^2}\right) = Nk_B\left(\frac{\varepsilon}{k_BT}\right)^2 e^{-\frac{\varepsilon}{k_BT}}$$

Nernst's Theorem (1906)
The Third Law of Thermodynamics

$$S(T)-S(0)=\int_0^T \frac{C_V(T')\,dT'}{T'}$$

A non-trivial issue – what's the value of ***S*(0)**?

The answer is provided by Q.M. (discreteness of quantum states), it cannot be deduced from the other laws of thermodynamics – thus, ***the third law***:

Nernst's Theorem: The entropy of a system at ***T* = 0** is a well-defined constant. For any processes that bring a system at ***T* = 0** from one equilibrium state to another, Δ ***S* = 0** .

This is because a system at ***T* = 0** exists in its ground state, so that its entropy is determined only by the degeneracy of the ground state.

$$S(0)=k_B\ln\Omega(0)$$

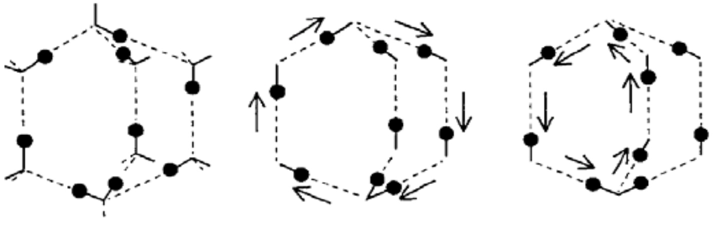
In other words, ***S*(*T*)** approaches a finite limit at ***T* = 0** , which does not depend on specifics of processes that brought the system to the ***T* = 0** state.

A special case – systems with ***unique ground state***, such as elementary crystals : ***S*(0) = 0** (**Ω = 1**). However, the claim that ***S*(0)** is "usually" zero or negligible is ***wrong***.

Residual Entropy

If ***S*(0) ≠ 0**, it’s called **residual entropy**.

1. For compounds, for example, there is frequently a significant amount of entropy that comes from a multiplicity of possible molecular orientations in the crystal (degeneracy of the ground state), ***even at absolute zero***.



Jisoon Ihm J. Phys. A: Math. Gen. **29** (1996) L1–L7

Structure of the hexagonal ice: ● - H atoms, --- - covalent O-H bonds, - - - - weak H bonds. Six H atoms can “tunnel” simultaneously through a potential barrier.


nature

ARTIFICIAL SPIN ICE

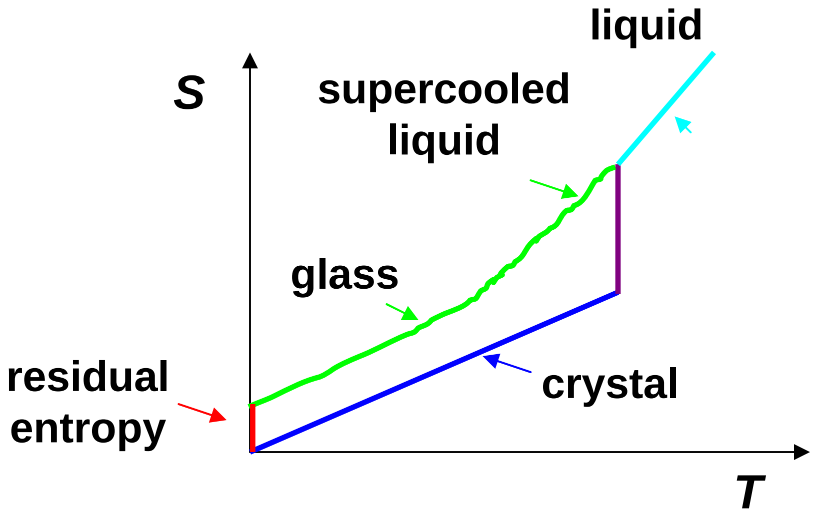
Frustration by design

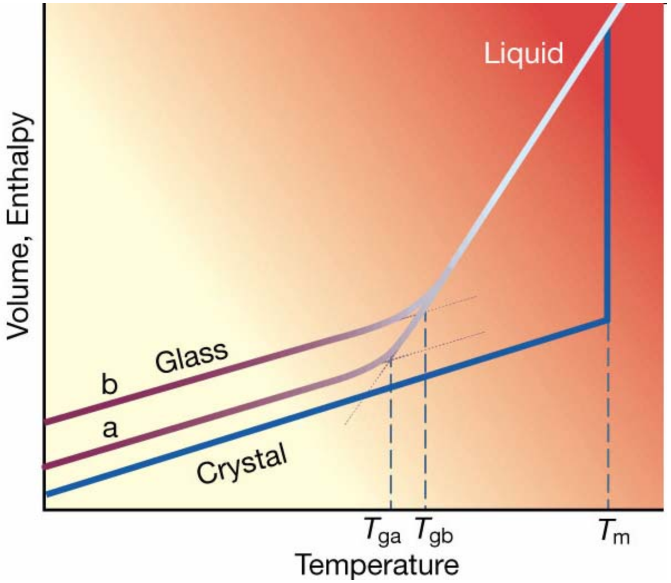
Wang et al, nature, 439, 303 (2006)

Residual Entropy (cont.)

2. Nernst's Theorem applies to the equilibrium states only!

Glasses aren't really in equilibrium, the relaxation time – huge. They do not have a well-defined ***T*** or ***C_V*.** Glasses have a particularly large entropy at ***T* = 0.**





Debenedetti & Stillinger, Nature (2001)

Example (Pr. 3.14)

For a mole of aluminum, $\boldsymbol{C_V = aT + bT^3}$ at $\boldsymbol{T} < 50$ K (**a** = $1.35{\cdot}10^{-3}$ J/K^2, **b** = $2.48{\cdot}10^{-5}$ J/K^4). The linear term – due to mobile electrons, the cubic term – due to the crystal lattice vibrations. Find ***S*(*T*)** and evaluate the entropy at ***T*** = 1K,10 K.

$$S(T) = \int_0^T \frac{C_V(T')\,dT'}{T'} = \int_0^T \frac{\left(aT' + bT'^3\right)dT'}{T'} = aT + \frac{b}{3}T^3$$

***T* = 1K**

$$S(1K) = 1.35\cdot 10^{-3}\ \mathrm{J/K^2} \times 1\mathrm{K} + \frac{1}{3}2.48\cdot 10^{-5}\ \mathrm{J/K^4} \times 1\mathrm{K}^3 = 1.36\cdot 10^{-3}\ \mathrm{J/K}$$

- at low ***T***, nearly all the entropy comes from the mobile electrons

***T* = 10K**

$$S(10K) = 1.35\cdot 10^{-3}\ \mathrm{J/K^2} \times 10\mathrm{K} + \frac{1}{3}2.48\cdot 10^{-5}\ \mathrm{J/K^4} \times 10^3\mathrm{K}^3 = 2.18\cdot 10^{-2}\ \mathrm{J/K}$$

- most of the entropy comes from lattice vibrations

$$\frac{S(1K)}{k_B} = \frac{1.35\cdot 10^{-3}\ \mathrm{J/K}}{1.38\cdot 10^{-23}\ \mathrm{J/K}} \approx 10^{20} \qquad \frac{S(10K)}{k_B} = \frac{2.18\cdot 10^{-2}\ \mathrm{J/K}}{1.38\cdot 10^{-23}\ \mathrm{J/K}} \approx 1.6\cdot 10^{21}$$

- much less than the # of particles, most degrees of freedom are still frozen out.

C → 0 as T → 0

$$S(T)-S(0)=\int_0^T \frac{C_V(T')\,dT'}{T'} \qquad C(T)\to 0 \quad \text{as} \quad T\to 0$$

For example, let's fix ***P*** :

$$\delta Q = C_P(T)dT \qquad \int_0^T \frac{\delta Q}{T'} = \int_0^T \frac{C_P(T')\,dT'}{T'}$$

\- finite, ∴ **$C_P(0) = 0$**

Similar, considering ***V* = const** **- $C_V(0) = 0$** .

Thus, the specific heat must be a function of ***T***. We know that at high ***T***, ***C_V*** approaches a universal temperature-independent limit that depends on ***N*** and # of degrees of freedom. This high - ***T*** behavior cannot persist down to ***T* = 0** – quantum effects will come into play.