In Lecture 4, we took a giant step towards the understanding why certain processes in macrosystems are irreversible. Our approach was founded on the following ideas:

- Each accessible microstate of an isolated system is equally probable (the fundamental assumption).
- Every macrostate has a countable number of microstates (follows from Q.M.).
- The probability of a macrostate is proportional to its multiplicity. When systems get large, multiplicities get outrageously large.

On this basis, we will introduce the concept of entropy and discuss the Second Law of Thermodynamics.
Our plan:

As our point of departure, we’ll use the models of an Einstein solid. We have already discussed one advantage of this model – “discrete” degrees of freedom. Another advantage – by considering two interacting Einstein solids, we can learn about the energy exchange between these two systems. In this respect, the two-state paramagnet model is less convenient: (a) an external magnetic field is needed to remove the degeneracy of different macrostates, and (b) the spectrum is “limited” in energy.

By using our statistical approach, we’ll introduce the concept of macropartition (a macrostate of a combined system of two interacting Einstein solids) and identify the most probable macropartition after reaching an equilibrium;

We’ll introduce the entropy as a measure of the multiplicity of a given macropartition

The Second Law of Thermodynamics
Two Interacting Einstein Solids, Macropartitions

Suppose that we bring two Einstein solids $A$ and $B$ (two sub-systems with $N_A$, $U_A$ and $N_B$, $U_B$) into thermal contact, to form a larger isolated system. What happens to these solids (macroscopically) after they have been brought into contact?

The combined system –

$$N = N_A + N_B, \quad U = U_A + U_B$$

Macropartition: a given pair of macrostates for sub-systems $A$ and $B$ that are consistent with conservation of the total energy $U = U_A + U_B$.

Different macropartitions amount to different ways that the energy can be macroscopically divided between the sub-systems.

Example: the pair of macrostates where $U_A = 2\varepsilon$ and $U_B = 4\varepsilon$ is one possible macropartition of the combined system with $U = 6\varepsilon$.

As time passes, the system of two solids will randomly shift between different microstates consistent with the constraint that $U =$ const.

Question: what would be the most probable macropartition for given $N_A, N_B, \text{ and } U$?
Problem:

Consider the system consisting of two Einstein solids in thermal contact. A certain macropartition has a multiplicity of $6 \cdot 10^{1024}$, while the total number of microstates available to the system in all macropartitions is $3 \cdot 10^{1034}$. What is the probability to find the system in this macropartition?

Imagine that the system is initially in the macropartition with a multiplicity of $6 \cdot 10^{1024}$. Consider another macropartition of the same system with a multiplicity of $6 \cdot 10^{1026}$. If we look at the system a short time later, how many more times likely is it to have moved to the second macropartition than to have stayed with the first?
The Multiplicity of Two Sub-Systems Combined

The probability of a macropartition is proportional to its multiplicity:

\[ \Omega_{AB} = \Omega_A \times \Omega_B \]

**Example:** two one-atom “solids” into thermal contact, with the total \( U = 6\varepsilon \).

Possible macropartitions for \( N_A = N_B = 3 \), \( U = q_A + q_B = 6\varepsilon \)

<table>
<thead>
<tr>
<th>Macropartition</th>
<th>( U_A )</th>
<th>( U_B )</th>
<th>( \Omega_A )</th>
<th>( \Omega_B )</th>
<th>( \Omega_{AB} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 : 6</td>
<td>0 ( \varepsilon )</td>
<td>6 ( \varepsilon )</td>
<td>1</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>1 : 5</td>
<td>1 ( \varepsilon )</td>
<td>5 ( \varepsilon )</td>
<td>3</td>
<td>21</td>
<td>63</td>
</tr>
<tr>
<td>2 : 4</td>
<td>2 ( \varepsilon )</td>
<td>4 ( \varepsilon )</td>
<td>6</td>
<td>15</td>
<td>90</td>
</tr>
<tr>
<td>3 : 3</td>
<td>3 ( \varepsilon )</td>
<td>3 ( \varepsilon )</td>
<td>10</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>4 : 2</td>
<td>4 ( \varepsilon )</td>
<td>2 ( \varepsilon )</td>
<td>15</td>
<td>6</td>
<td>90</td>
</tr>
<tr>
<td>5 : 1</td>
<td>5 ( \varepsilon )</td>
<td>1 ( \varepsilon )</td>
<td>21</td>
<td>3</td>
<td>63</td>
</tr>
<tr>
<td>6 : 0</td>
<td>6 ( \varepsilon )</td>
<td>0 ( \varepsilon )</td>
<td>28</td>
<td>1</td>
<td>28</td>
</tr>
</tbody>
</table>

Grand total # of microstates:

\[
\frac{(U / \varepsilon + N - 1)!}{(U / \varepsilon)!(N - 1)!} = \frac{(6 + 6 - 1)!}{(6)!(6 - 1)!} = 462
\]
Where is the Maximum? The Average Energy per Atom

Let’s explore how the macropartition multiplicity for two sub-systems \( A \) and \( B \) \((N_A, N_B, \varepsilon_A = \varepsilon_B = \varepsilon)\) in thermal contact depends on the energy of one of the sub-systems:

The high-\( T \) limit \((q \gg N)\):

\[
\Omega_A(N_A, U_A) = \left(\frac{eU_A}{N_A \varepsilon}\right)^{N_A}, \quad \Omega_B(N_B, U_B) = \left(\frac{eU_B}{N_B \varepsilon}\right)^{N_B}
\]

\[
\Omega_{AB} = \Omega_A(N_A, U_A) \times \Omega_B(N_B, U_B) = \left(\frac{eU_A}{N_A \varepsilon}\right)^{N_A} \left(\frac{e(U-U_A)}{N_B \varepsilon}\right)^{N_B}
\]

\[
\frac{d\Omega_{AB}}{dU_A} = N_A \left(\frac{eU_A}{N_A \varepsilon}\right)^{N_A-1} \frac{e}{N_A \varepsilon} \left(\frac{e(U-U_A)}{N_B \varepsilon}\right)^{N_B} + N_B \left(\frac{eU_A}{N_A \varepsilon}\right)^{N_A} \left(\frac{e(U-U_A)}{N_B \varepsilon}\right)^{N_B-1} \left(-\frac{e}{N_B \varepsilon}\right) = 0
\]

For two systems in thermal contact, the equilibrium (most probable) macropartition of the combined system is the one where **the average energy per atom in each system is the same** (the basis for introducing the temperature).

For two identical sub-systems \((N_A = N_B)\), \(\Omega_{AB}(U_A)\) is peaked at \(U_A = U_B = \frac{1}{2} U\):

\[
\begin{align*}
\Omega_A &\uparrow \\
U/2 &\quad U_A
\end{align*}
\]

\[
\begin{align*}
\Omega_B &\uparrow \\
U/2 &\quad U_A
\end{align*}
\]

\[
\begin{align*}
\Omega_{AB} &\uparrow \\
U/2 &\quad U_A
\end{align*}
\]

At home: find the position of the maximum of \(\Omega_{AB}(U_A)\) for \(N_A = 200, N_B = 100, U = 180\)
Sharpness of the Multiplicity Function

How sharp is the peak? Let’s consider small deviations from the maximum for two identical sub-systems:

\[ U_A = \frac{U}{2} (1+x) \quad U_B = \frac{U}{2} (1-x) \quad (x \ll 1) \]

\[ \Omega_{AB} \propto (U_A)^N (U_B)^N = \left( \frac{U}{2} \right)^{2N} (1-x)^N (1+x)^N \propto \Omega_{AB}^{eq} (1-x^2)^N \]

**Example:** \( N = 100,000 \quad x = 0.01 \quad \Rightarrow \quad (0.9999)^{100,000} \approx 4.5 \cdot 10^{-5} \quad \Leftrightarrow \quad 1 \)

More rigorously (p. 65):

\[ \Omega_{AB} = \left( \frac{e}{N\varepsilon} \right)^{2N} (U_A)^N (U_B)^N \propto (U/2)^N \times (U/2)^N \exp \left[ -N \left( \frac{\Delta U}{U/2} \right)^2 \right] \]

a Gaussian function

The peak width:

\[ N \left( \frac{\Delta U}{U/2} \right)^2 = 1 \quad \Rightarrow \quad \Delta U = \frac{1}{\sqrt{N}} \frac{U}{2} \]

When the system becomes large, the probability as a function of \( U_A \) (macropartition) becomes very sharply peaked.
Consider the system consisting of two Einstein solids $P$ and $Q$ in thermal equilibrium. Assume that we know the number of atoms in each solid and $\varepsilon$. What do we know if we also know

(a) the quantum state of each atom in each solid?

(b) the total energy of each of the two solids?

(c) the total energy of the combined system?

<table>
<thead>
<tr>
<th></th>
<th>the system’s macrostate</th>
<th>the system’s microstate</th>
<th>the system’s宏观partition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>(b)</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>(c)</td>
<td>X</td>
<td></td>
<td>X (fluctuations)</td>
</tr>
</tbody>
</table>
Implications? Irreversibility!

The vast majority of microstates are in macropartitions close to the most probable one (in other words, because of the “narrowness” of the macropartition probability graph). Thus,

(a) If the system is not in the most probable macropartition, it will rapidly and inevitably move toward that macropartition. The reason for this “directionality” (irreversibility): there are far more microstates in that direction than away. This is why energy flows from “hot” to “cold” and not vice versa.

(b) It will subsequently stay at that macropartition (or very near to it), in spite of the random shuffling of energy back and forth between the two solids.

When two macroscopic solids are in thermal equilibrium with each other, completely random and reversible microscopic processes (leading to random shuffling between microstates) tend at the macroscopic level to push the solids inevitably toward an equilibrium macropartition (an irreversible macro behavior). Any random fluctuations away from the most likely macropartition are extremely small!
Problem:

Imagine that you discover a strange substance whose multiplicity is always 1, no matter how much energy you put into it. If you put an object made of this substance (sub-system \( A \)) into thermal contact with an Einstein solid having the same number of atoms but much more energy (sub-system \( B \)), what will happen to the energies of these sub-systems?

A. Energy flows from \( B \) to \( A \) until they have the same energy.

B. Energy flows from \( A \) to \( B \) until \( A \) has no energy.

C. No energy will flow from \( B \) to \( A \) at all.
Entropy

of a system in a given macrostate \((N, U, V... )\):

\[
S \equiv k_B \ln \Omega \left( N, U, V... \right)
\]

Units: J/K

The entropy is a **state function**, i.e. it depends on the macrostate alone and not on the path of the system to this macrostate.

Entropy is just another (more convenient) way of talking about multiplicity.

**Convenience:**
- reduces ridiculously large numbers to manageable numbers

**Examples:** for \(N \sim 10^{23}, \ \Omega \sim 10^{10^{23}}, \ \ln \Omega \sim 10^{23}\), being multiplied by \(k_B \sim 10^{-23}\), it gives
  \( S \sim 1\text{J/K} \).

The “inverse” procedure: the entropy of a certain macropartition is 4600\(k_B\).
What is the multiplicity of the macropartition?

\[
\Omega = e^{\frac{S}{k_B}} = e^{4600} \sim 10^{2000}
\]

if a system contains two or more interacting sub-systems having their own distinct macrostates, the total entropy of the combined system in a given macropartition is the sum of the entropies of the subsystems they have in that macropartition:

\[
\Omega_{AB} = \Omega_A \times \Omega_B \times \Omega_C \times ... \Rightarrow \ S_{AB} = S_A + S_B + S_C + ...
\]
Imagine that one macropartition of a combined system of two Einstein solids has an entropy of 1 J/K, while another (where the energy is more evenly divided) has an entropy of 1.001 J/K. How many times more likely are you to find the system in the second macropartition compared to the first?

\[
\frac{\text{Prob(mp2)}}{\text{Prob(mp1)}} = \frac{\Omega_2}{\Omega_1} = \frac{e^{S_2/k_B}}{e^{S_1/k_B}} \approx \frac{e^{0.72464 \cdot 10^{23}}}{e^{0.72536 \cdot 10^{23}}} = e^{7.2 \cdot 10^{19}}
\]
The Second Law 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. Thus,

The entropy of an isolated system never decreases.

(one of the formulations of the second law of thermodynamics).

( Is it really true that the entropy of an isolated system never decreases? consider a pair of very small Einstein solids. Why is this statement more accurate for large systems than small systems? )

Whatever increases the number of microstates will happen if it is allowed by the fundamental laws of physics and whatever constraints we place on the system.
“Whatever” - energy exchange, particles exchange, expansion of a system, etc.
Entropy and Temperature

To establish the relationship between $S$ and $T$, let’s consider two sub-systems, $A$ and $B$, isolated from the environment. The sub-systems are separated by a rigid membrane with finite thermal conductivity ($N_i$ and $V_i$ are fixed, thermal energy can flow between the sub-systems). The sub-systems – with the “quadratic” degrees of freedom ($S \sim U^{fn/2}$). For example, two identical Einstein solids ($N_A = N_B = N$) near the equilibrium macropartition ($U_A = U_B = U/2$):

$$\Omega_{AB} = \Omega_A (N, U_A) \times \Omega_B (N, U_B) = \left( \frac{e}{N \varepsilon} \right)^2 \left( U_A \right)^N \left( U_B \right)^N$$

$$S_{AB} = S_A + S_B = 2N \ln \left( \frac{e}{N \varepsilon} \right) + N \ln(U_A) + N \ln(U_B)$$

**Equilibrium:**

$$\frac{\partial S_{AB}}{\partial U_A} + \frac{\partial S_A}{\partial U_A} - \frac{\partial S_A}{\partial U_B} = 0 \quad \Rightarrow \quad \frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$$

Thus, when two solids are in equilibrium, the slope is the same for both of them.

On the other hand, when two solids are in equilibrium, they have the same temperature.

Units: $T$ – K, $S$ – J/K, $U$ - J
1. Note that the partial derivative in the definition of $T$ is calculated at $V=\text{const}$ and $N=\text{const}$. 

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

We have been considering the entropy changes in the processes where two interacting systems exchanged the thermal energy but the volume and the number of particles in these systems were fixed. In general, however, we need more than just one parameter to specify a macrostate:

$$S \equiv k_B \ln \Omega(U,V,N)$$

The physical meaning of the other two partial derivatives of $S$ will be considered in L.7.

2. The slope $\partial S / \partial U$ is \textit{inversely} proportional to $T$.

- the energy should flow from higher $T$ to lower $T$; in thermal equilibrium, $T_A$ and $T_B$ should be the same.

The sub-system with a larger $\partial S / \partial U$ (lower $T$) should receive energy from the sub-system with a smaller $\partial S / \partial U$ (higher $T$), and this process will continue until $\partial S_A / \partial U_A$ and $\partial S_B / \partial U_B$ become the same.
**Problems**

**Problem:** An object whose multiplicity is always 1, no matter what its thermal energy is has a temperature that: (a) is always 0; (b) is always fixed; (c) is always infinite.

**Problem:** Imagine that you discover a strange substance whose multiplicity is always 1, no matter how much energy you put into it. If you put an object made of this substance (sub-system \( A \)) into thermal contact with an Einstein solid having the same number of atoms but much more energy (sub-system \( B \)), what will happen to the energies of these sub-systems?

Energy flows from \( A \) to \( B \) until \( A \) has no energy – the temperature of sub-system \( A \) is infinitely high.

**Problem:** If an object has a multiplicity that decreases as its thermal energy increases (e.g., a two-state paramagnetic over a certain \( U \) range), its temperature would: (a) be always 0; (b) be always fixed; (c) be negative; (d) be positive.

\[
T \equiv \left( \frac{\partial S}{\partial U} \right)^{-1}_{V,N}
\]
Measuring Entropy

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

For $V=\text{const}$ and $N=\text{const}$:

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

- in L.7, 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 $S \equiv k_B \ln \Omega$.

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

By heating a cup of water (200g, $C_V = 840$ J/K) from $20^0\text{C}$ to $100^0\text{C}$, 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:

1. Find \( \Omega(U,V,N,...) \) – the most challenging step

2. \( S(U,V,N,...) = k_B \ln \Omega(U,V,N,...) \)

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

4. Solve for \( U = f(T,V,N,...) \)
An Einstein Solid: from $S(N,U)$ to $U(N,T)$ at high $T$

**High temperatures:**

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

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

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

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

$$U(N,T) = N k_B T$$

- in agreement with the equipartition theorem: the total energy should be $\frac{1}{2} k_B T$ 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:**

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

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

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

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

The low-$T$ heat capacity:

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

$$
C_V = \frac{\partial}{\partial T} \left( N\varepsilon \, e^{\frac{-\varepsilon}{k_B T}} \right) = N\varepsilon \, e^{\frac{-\varepsilon}{k_B T}} \left( \frac{\varepsilon}{k_B T^2} \right) = Nk_B \left( \frac{\varepsilon}{k_B T} \right)^2 e^{\frac{-\varepsilon}{k_B T}}
$$
Nernst’s Theorem (1906)
The Third Law of Thermodynamics

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

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, \( \Delta S = 0 \).

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.

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: \( S(0) = 0 \) (\( \Omega = 1 \)). However, the claim that \( S(0) \) is "usually" zero or negligible is **wrong**.
Residual Entropy

If $S(0) \neq 0$, 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.

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

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 $T = 0$. 
Example (Pr. 3.14)

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

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

\( T = 1\text{K} \)

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

- at low \( T \), nearly all the entropy comes from the mobile electrons

\( T = 10\text{K} \)

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

- most of the entropy comes from lattice vibrations

\[
\frac{S(1\text{K})}{k_B} = \frac{1.35 \cdot 10^{-3} \text{ J/K}}{1.38 \cdot 10^{-23} \text{ J/K}} \approx 10^{20} \quad \frac{S(10\text{K})}{k_B} = \frac{2.18 \cdot 10^{-2} \text{ J/K}}{1.38 \cdot 10^{-23} \text{ J/K}} \approx 1.6 \cdot 10^{21}
\]

- much less than the \# of particles, most degrees of freedom are still frozen out.
\[ S(T) - S(0) = \int_0^T \frac{C_V(T')dT'}{T'} \quad C(T) \to 0 \text{ as } T \to 0 \]

For example, let’s fix \( P \):

\[ \delta Q = C_p(T)dT \int_0^T \frac{\delta Q}{T'} = \int_0^T \frac{C_p(T')dT'}{T'} \quad \text{finite, } \therefore \quad C_p(0) = 0 \]

Similar, considering \( V = \text{const} \) - \( C_v(0) = 0 \).

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.