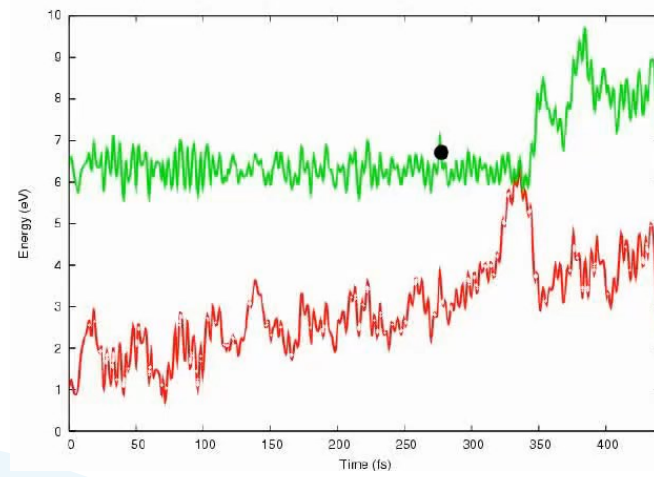
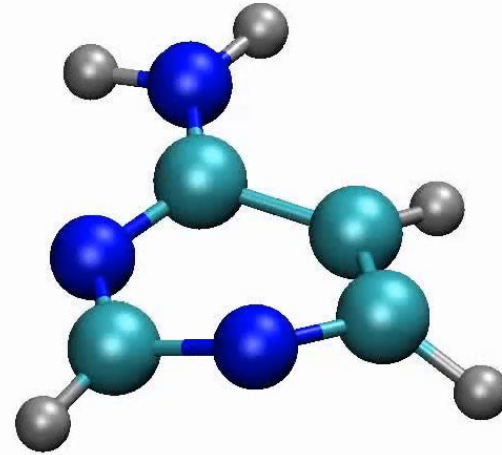
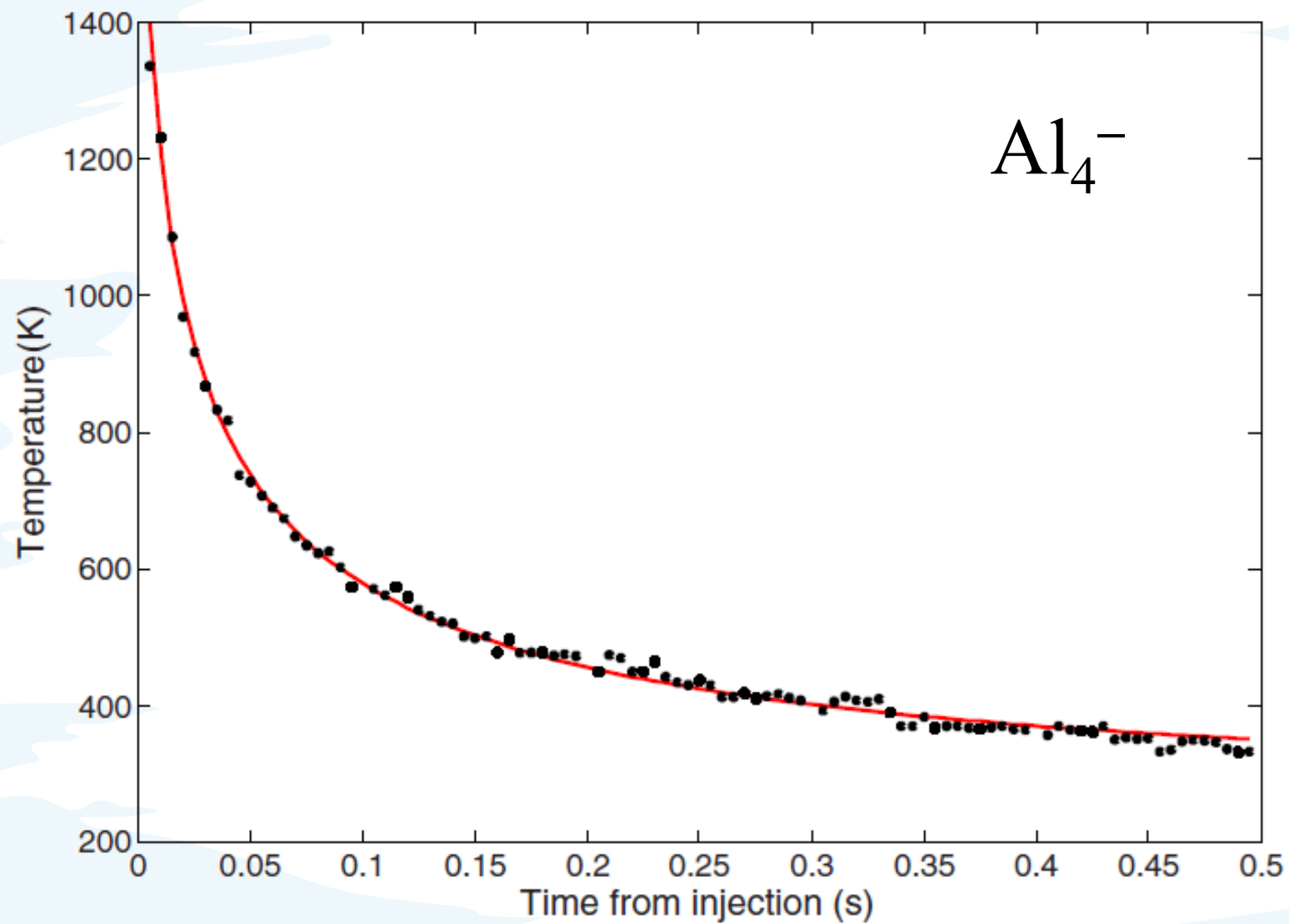


What is the temperature of an isolated molecule in a vacuum?

Mario Barbatti

*Aix Marseille University, Institut de Chimie Radicalaire, Marseille
Institut Universitaire de France, Paris*





THE NEAR-INFRARED CONTINUUM EMISSION OF VISUAL REFLECTION NEBULAE

K. SELLGREN^{1,2}

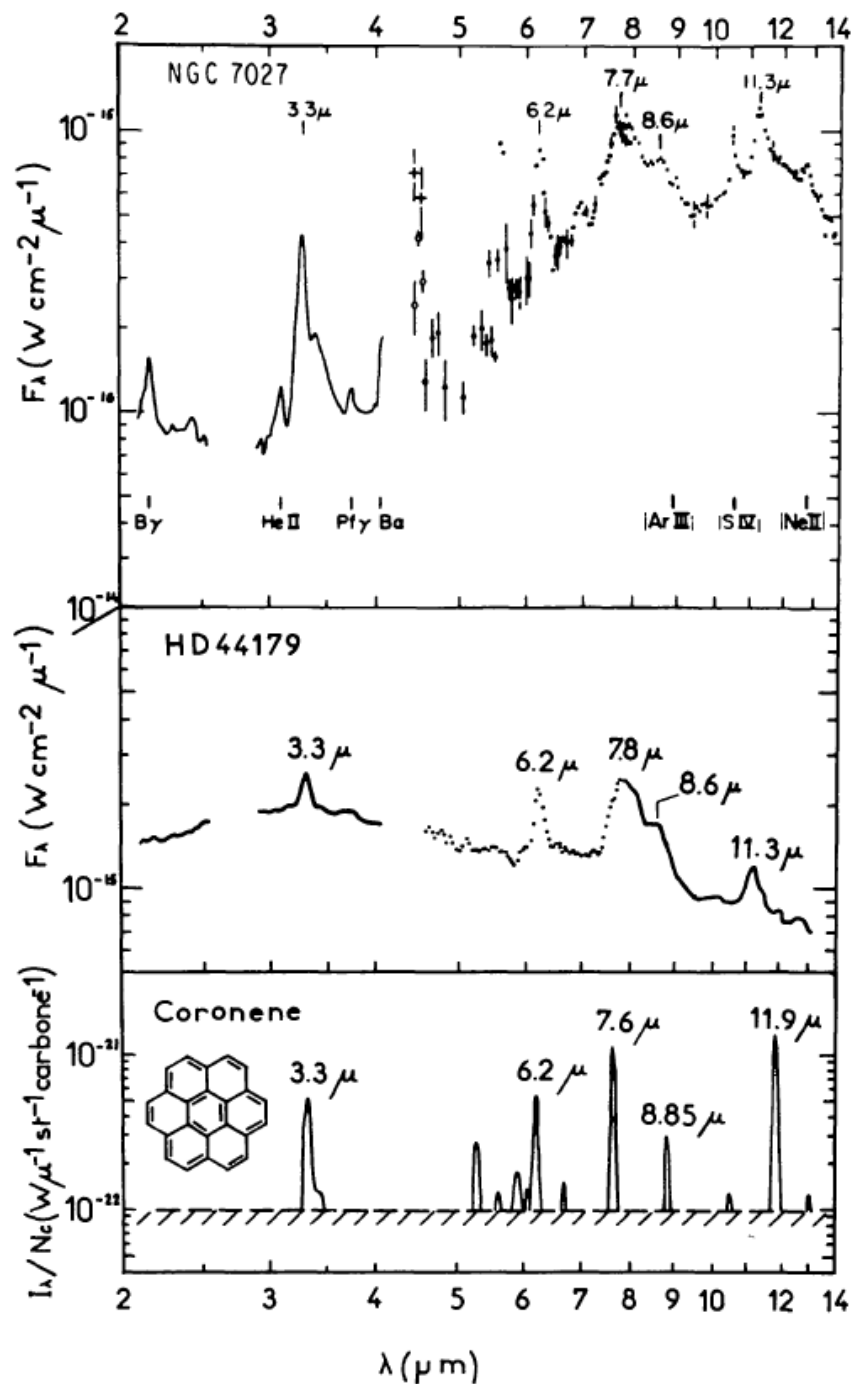
California Institute of Technology

Received 1983 May 9; accepted 1983 August 8

ABSTRACT

The near-infrared emission of the visual reflection nebulae NGC 7023, 2023, and 2068 is found to consist of a smooth continuum from 1.25 to 4.8 μm , characterized by a color temperature of ~ 1000 K, and strong emission features at 3.3 and 3.4 μm . The spectrum is the same in all three sources, and is independent of position over regions 0.4–0.9 pc in diameter within each source. The 2.2 μm surface brightness distributions in NGC 7023 and 2023 agree well with the distributions of visual reflected light. The near-infrared emission, however, cannot be explained by reflected light, fluorescence, faint stars, free-free emission, or by thermal emission from dust in equilibrium with the stellar radiation field.

A model is proposed in which the emission is due to thermal emission from very small grains (radius ~ 10 Å) which are briefly heated to ~ 1000 K by absorption of individual ultraviolet photons. This model explains the agreement between near-infrared and visual surface brightness distributions, and the constancy of the energy distribution with offset from the central stars. The number of grains with ~ 10 Å radius required by the observations is in agreement with the numbers expected from an extrapolation of the grain size distribution of Mathis, Rumpl, and Nordsieck to smaller grain sizes.



Interstellar PAH

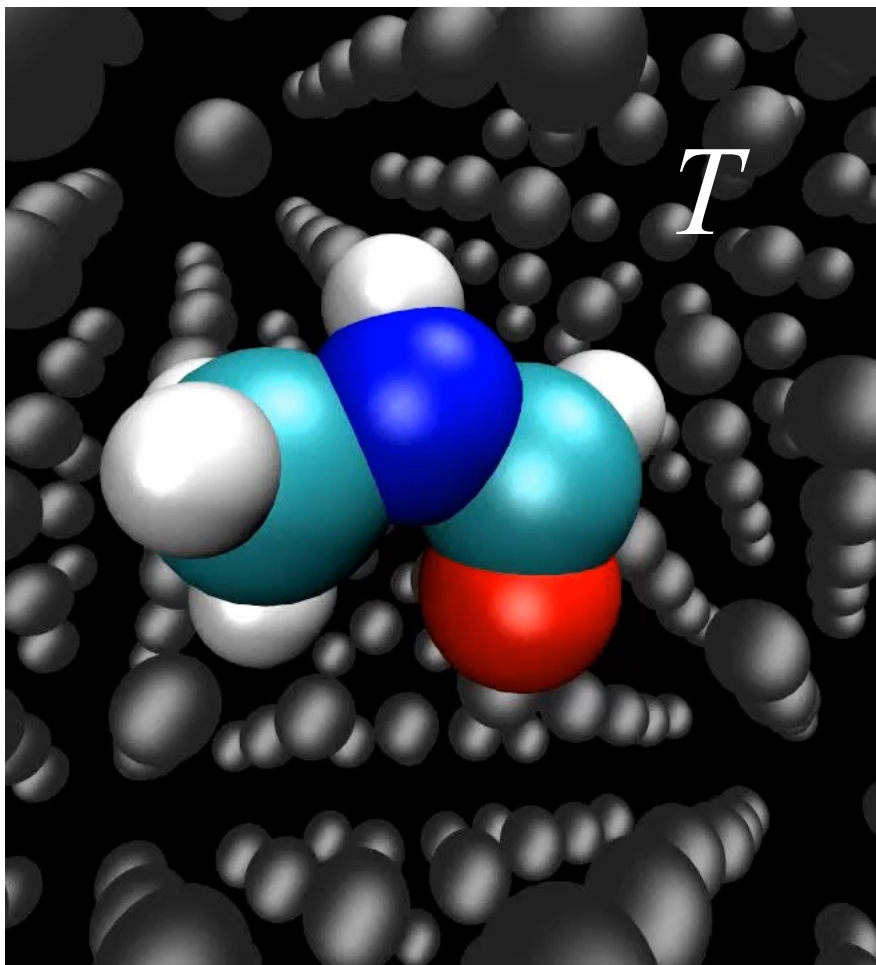
- $T_{peak} = 950 \pm 150 \text{ K}$
- UV absorption = 6 eV
- C_v for carbon atoms

Number of carbon atoms ~ 60

Leger; Puget. *Astron Astrophys* **1984**, 500, 279

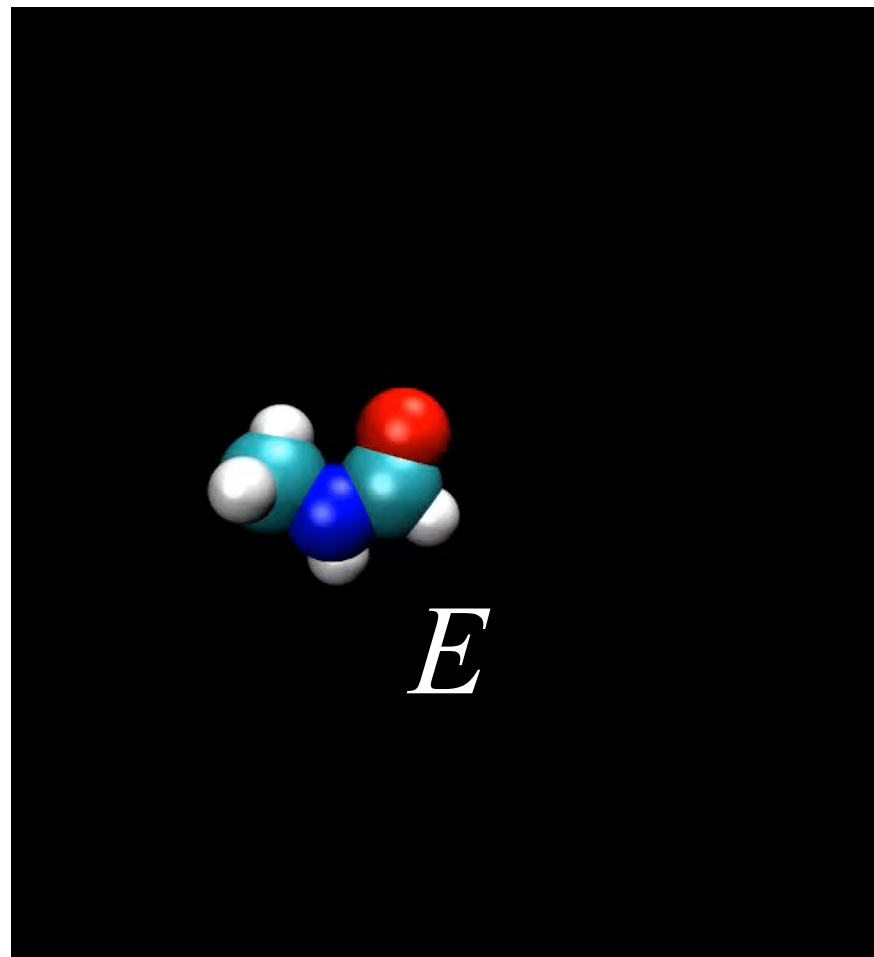
Canonical ensemble

$$E(T) = E_{\text{ZP}} + \sum_k \frac{h\nu_k}{e^{h\nu_k/k_B T} - 1}$$



Microcanonical ensemble

$$T(E) = ?$$



Classical limit ($E_{kin} = Nk_B T / 2$)

$$T(E) \approx \frac{E}{Nk_B}$$

Berry; Smirnov. *Phys-Uspekhi* **2009**, 52, 137
Belega et al. *Chem Phys Lett* **2010**, 496, 167

Andersen-Bonderup-Hansen model

$$T(E) \approx \frac{E}{(N-1)k_B}$$

Andersen; Bonderup; Hansen. *J Chem Phys*
2001, 114, 6518

We need a theory of the microcanonical temperature of an isolated molecule based on solid physical statistical grounds and spanning a broader energy domain.



Principles of Statistical Physics

Temperature

$$T = \left(\frac{\partial S}{\partial E} \right)^{-1}$$

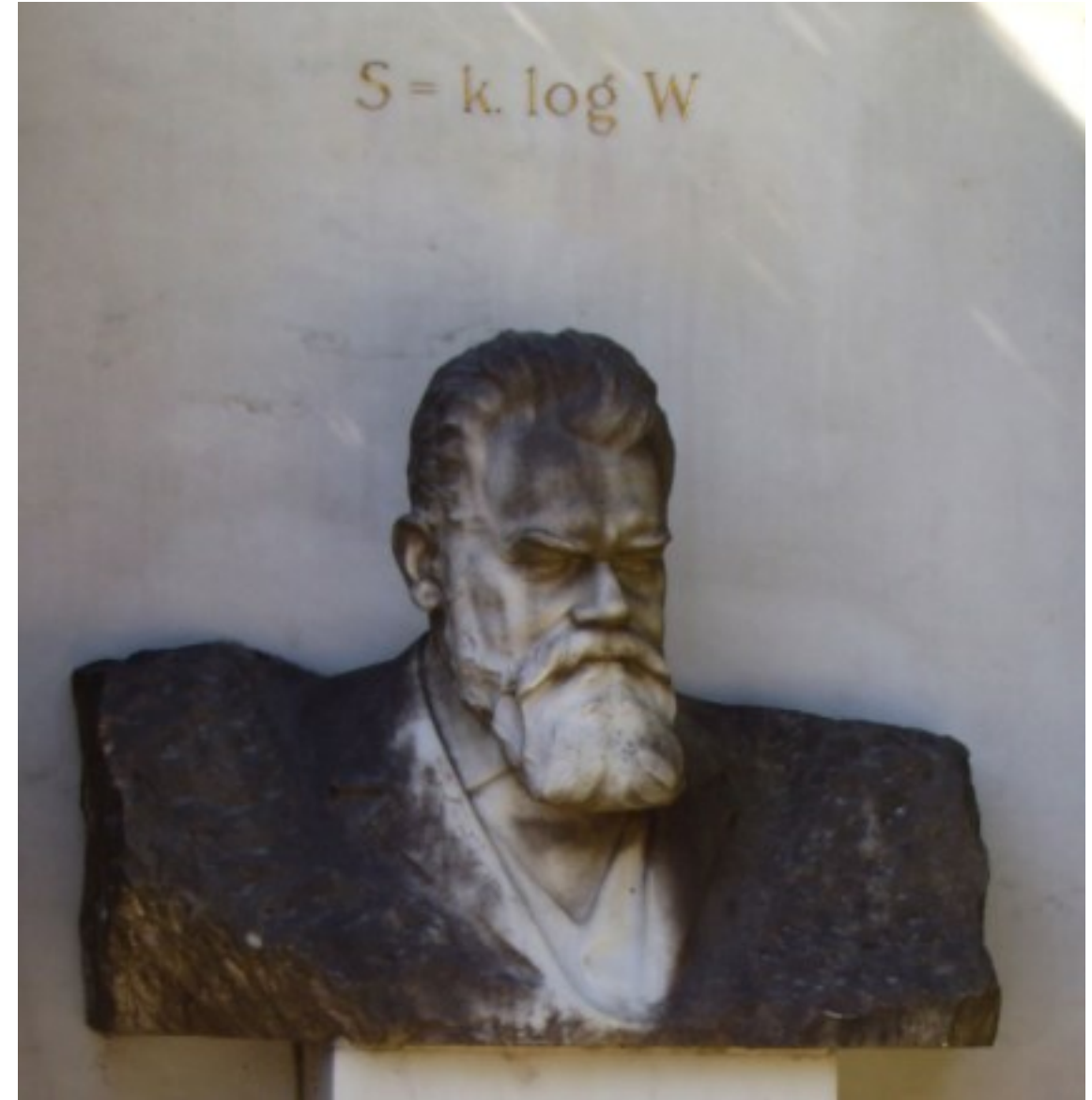
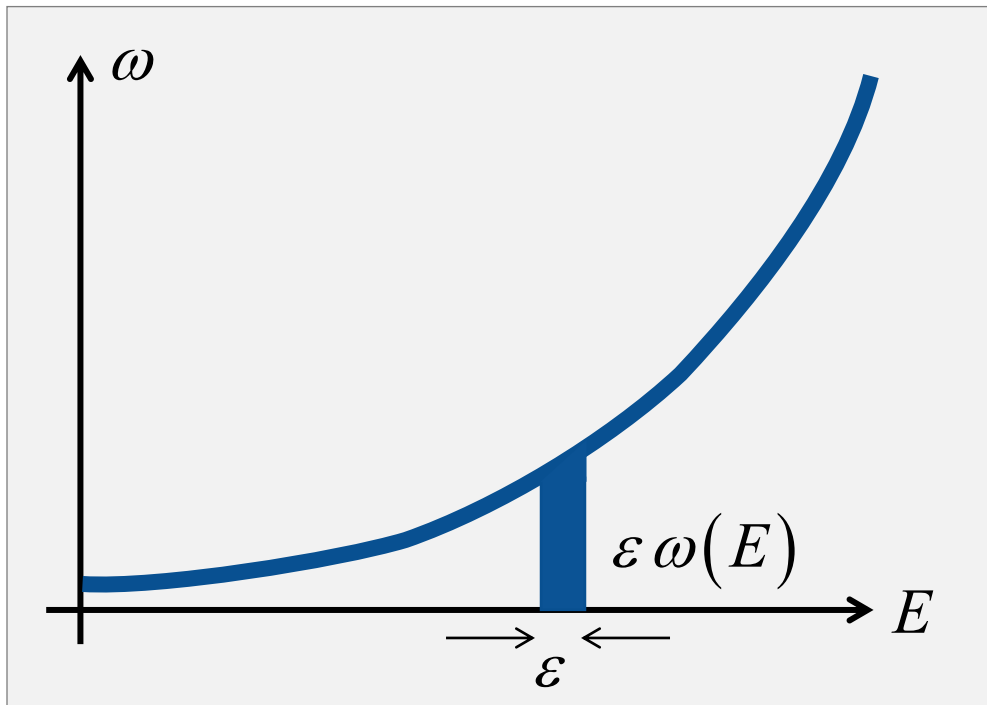
Heat Capacity

$$C = \left(\frac{\partial T}{\partial E} \right)^{-1}$$

Boltzmann entropy

$$S_B(E) = k_B \ln[\varepsilon \omega(E)]$$

$$\omega(E) = \text{Tr}[\delta(E - H(\xi))]$$



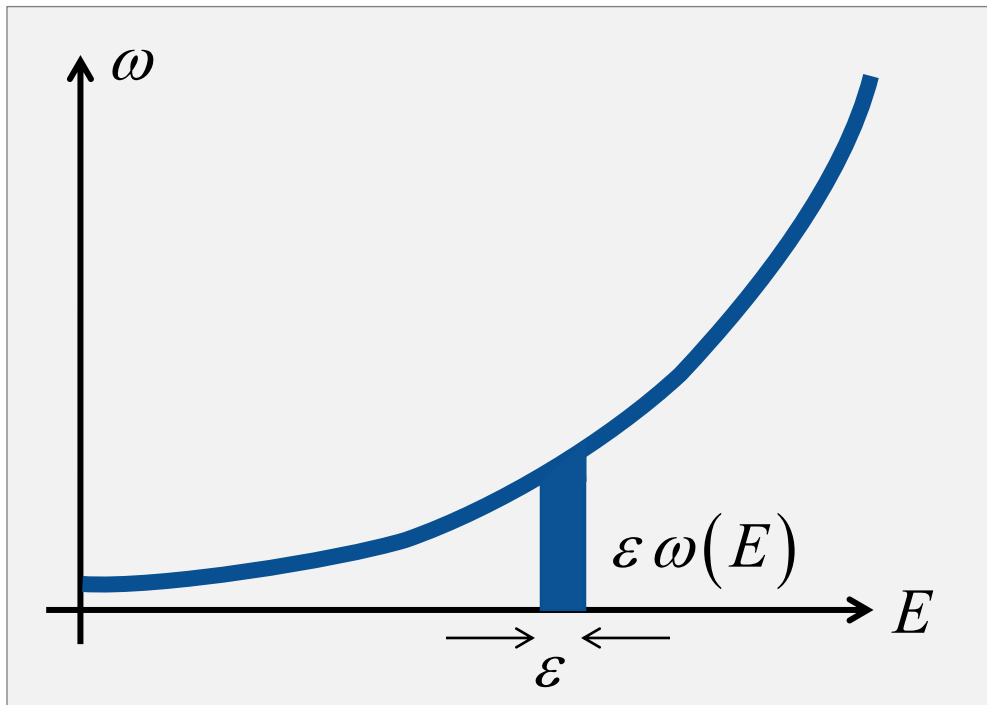
which has been demonstrated in Chapter X, and which relates to a microcanonical ensemble, $\overline{A_1}_\epsilon$ denoting the average value of A_1 in such an ensemble, corresponds precisely to the thermodynamic equation, except for the sign of average applied to the external forces. But as these forces are not entirely determined by the energy with the external coördinates, the use of average values is entirely germane to the subject, and affords the readiest means of getting perfectly determined quantities. These averages, which are taken for a microcanonical ensemble, may seem from some points of view a more simple and natural conception than those which relate to a canonical ensemble. Moreover, the energy, and the quantity corresponding to entropy, are free from the sign of average in this equation.

The quantity in the equation which corresponds to entropy is $\log V$, the quantity V being defined as the extension-in-phase within which the energy is less than a certain limiting value (ϵ). This is certainly a more simple conception than the average value in a canonical ensemble of the index of probability of phase. $\log V$ has the property that when it is constant

Boltzmann entropy

$$S_B(E) = k_B \ln[\varepsilon \omega(E)]$$

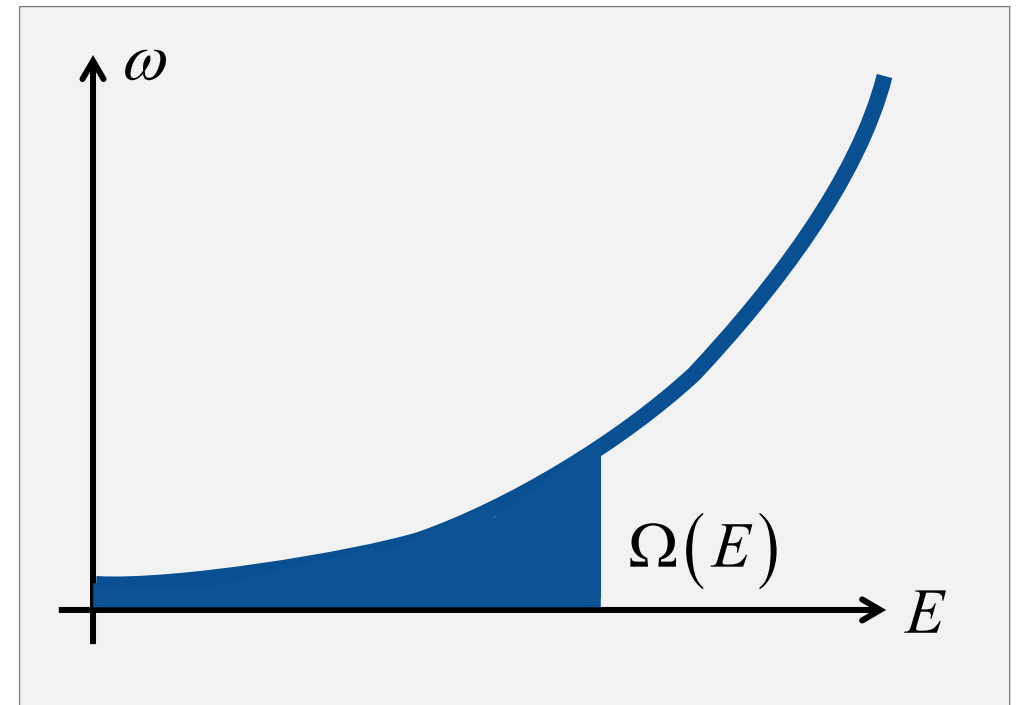
$$\omega(E) = \text{Tr}[\delta(E - H(\xi))]$$



Gibbs volume entropy

$$S_G(E) = k_B \ln[\Omega(E)]$$

$$\Omega(E) = \text{Tr}[\Theta(E - H(\xi))]$$





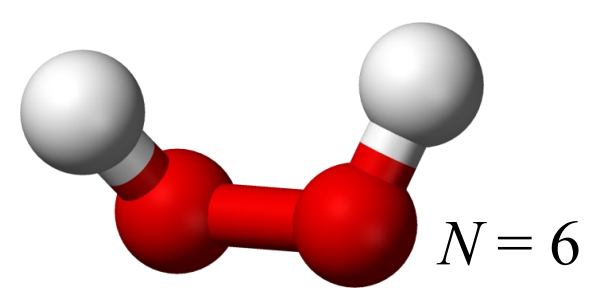
Molecular model

Quantum harmonic approximation

- Isolated molecule in a vacuum
- Rigid molecule
- No external fields
- Single electronic state

Then, the molecule's energy is

$$E_{\xi} = E_{ZP} + \sum_{k=1}^N n_k h\nu_k \quad (n_k = 0, 1, \dots)$$



$$E_{\xi} = E_{ZP} + \sum_k n_k h\nu_k$$

Frequencies (cm^{-1})

$$\nu_1 = 346$$

$$\nu_2 = 956$$

$$\nu_3 = 1330$$

$$\nu_4 = 1469$$

$$\nu_5 = 3704$$

$$\nu_6 = 3709$$

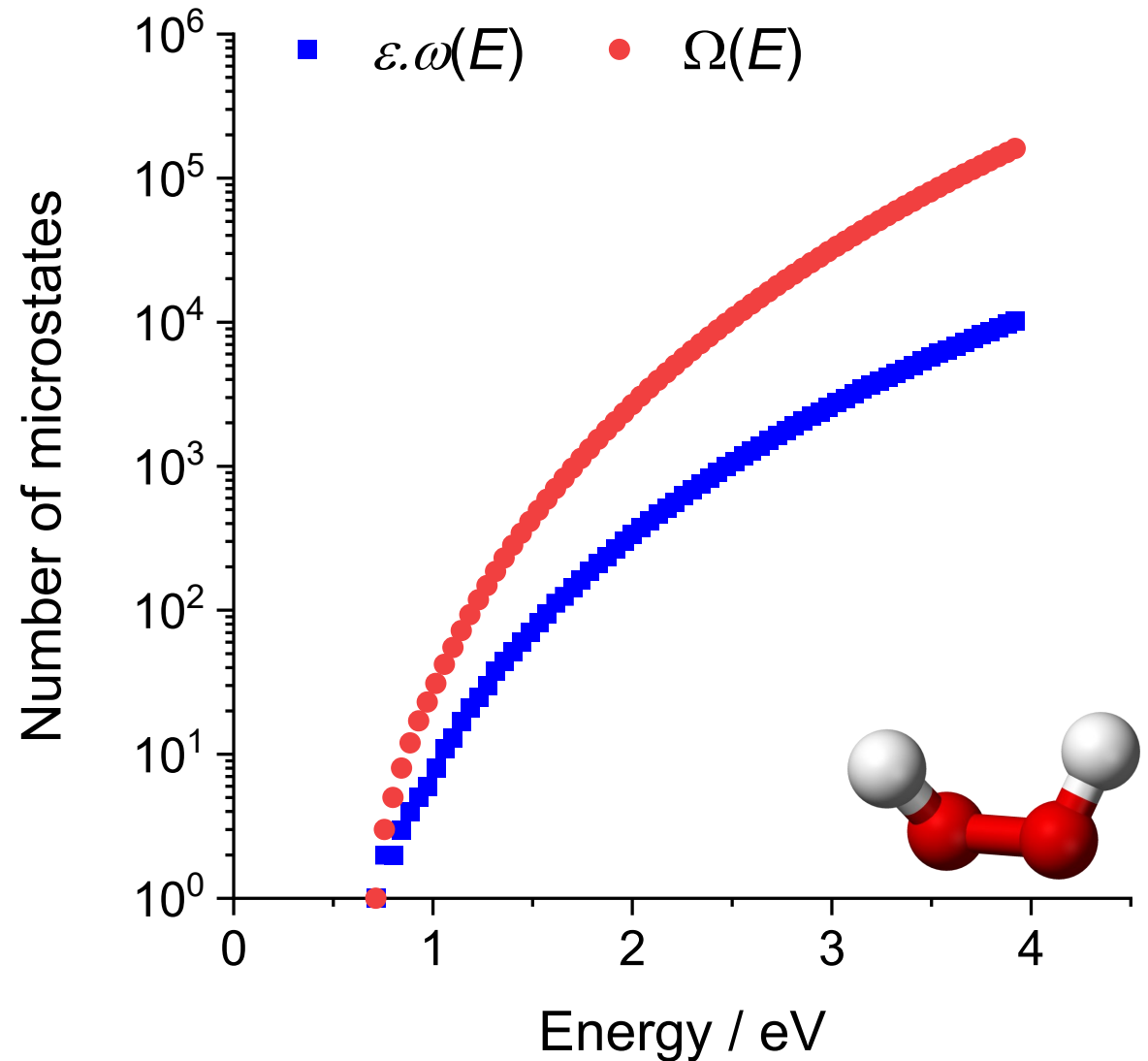
n_1	n_2	n_3	n_4	n_5	n_6	E (au)
0	0	0	0	0	0	0.026232
1	0	0	0	0	0	0.027809
2	0	0	0	0	0	0.029385
3	0	0	0	0	0	0.030961
4	0	0	0	0	0	0.032538
:						
0	1	3	1	1	0	0.072345
1	1	3	1	1	0	0.073921
2	1	3	1	1	0	0.075497
3	1	3	1	1	0	0.077074
4	1	3	1	1	0	0.078650
5	1	3	1	1	0	0.080226
:						
1	0	0	0	1	6	0.146080
0	0	0	0	0	7	0.144524
1	0	0	0	0	7	0.146101
:						

Number of microstates

■ $h\nu_1 \omega(E_k) = \sum_{n_1} \cdots \sum_{n_N} E_{n_1 \cdots n_N} \eta(E_k)$

$$\eta(E_k) = \begin{cases} 1 & \text{if } E_k \leq E_{n_1 \cdots n_N} < E_k + h\nu_1 \\ 0 & \text{otherwise} \end{cases}$$

■ $\Omega(E_k) = \sum_{j=0}^k h\nu_1 \omega(E_j)$

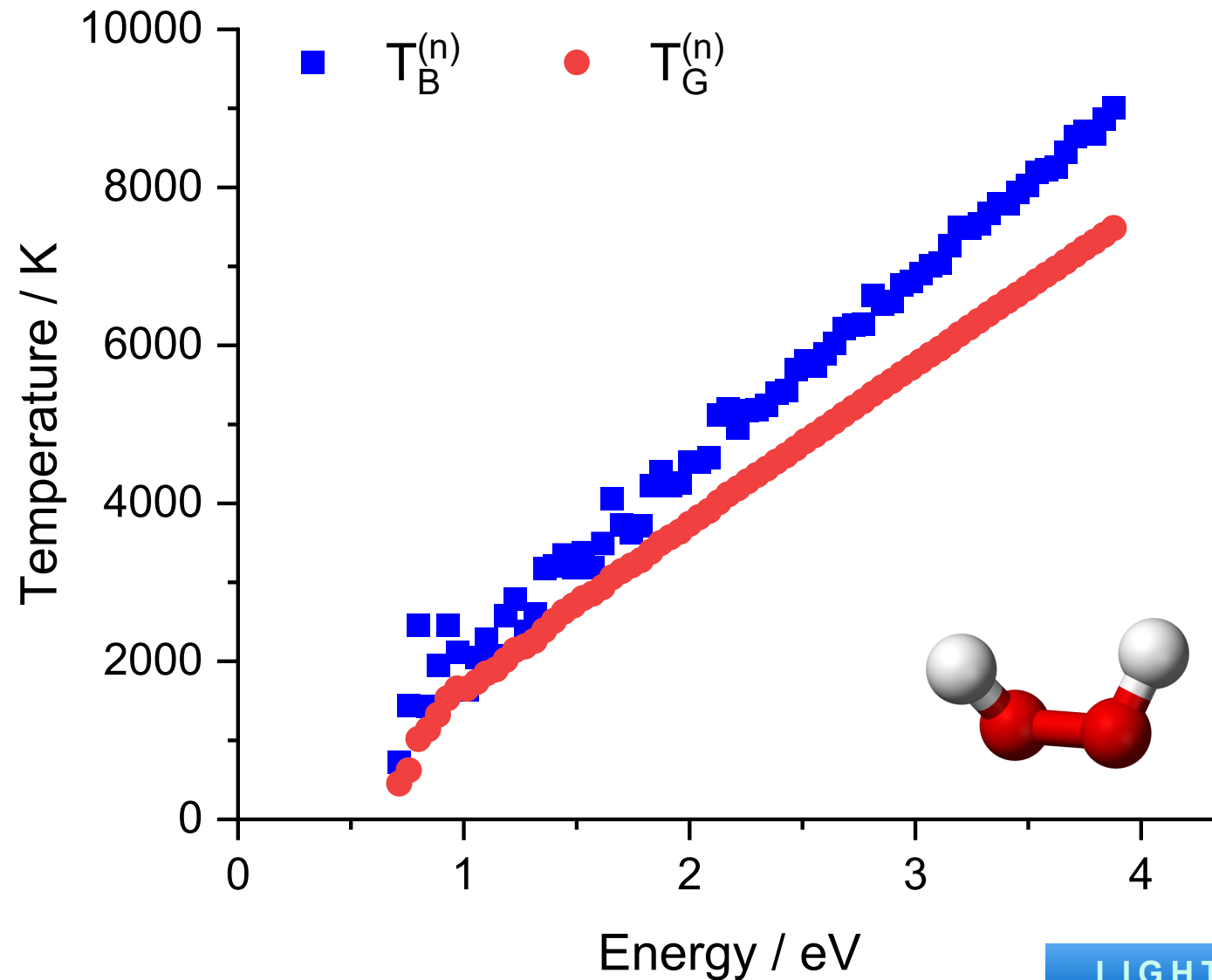


Temperature

$$T = \left(\frac{\partial S}{\partial E} \right)^{-1}$$

$$S_B(E) = k_B \ln[\varepsilon \omega(E)]$$

$$S_G(E) = k_B \ln[\Omega(E)]$$



Between E and $E + \varepsilon$, how many solutions does this equation have?

$$E_{\xi} = E_{ZP} + \sum_k n_k h\nu_k$$

The solution is known only for the degenerated problem:

$$E_M = E_{ZP} + Mh\bar{\nu}$$



The degenerated problem

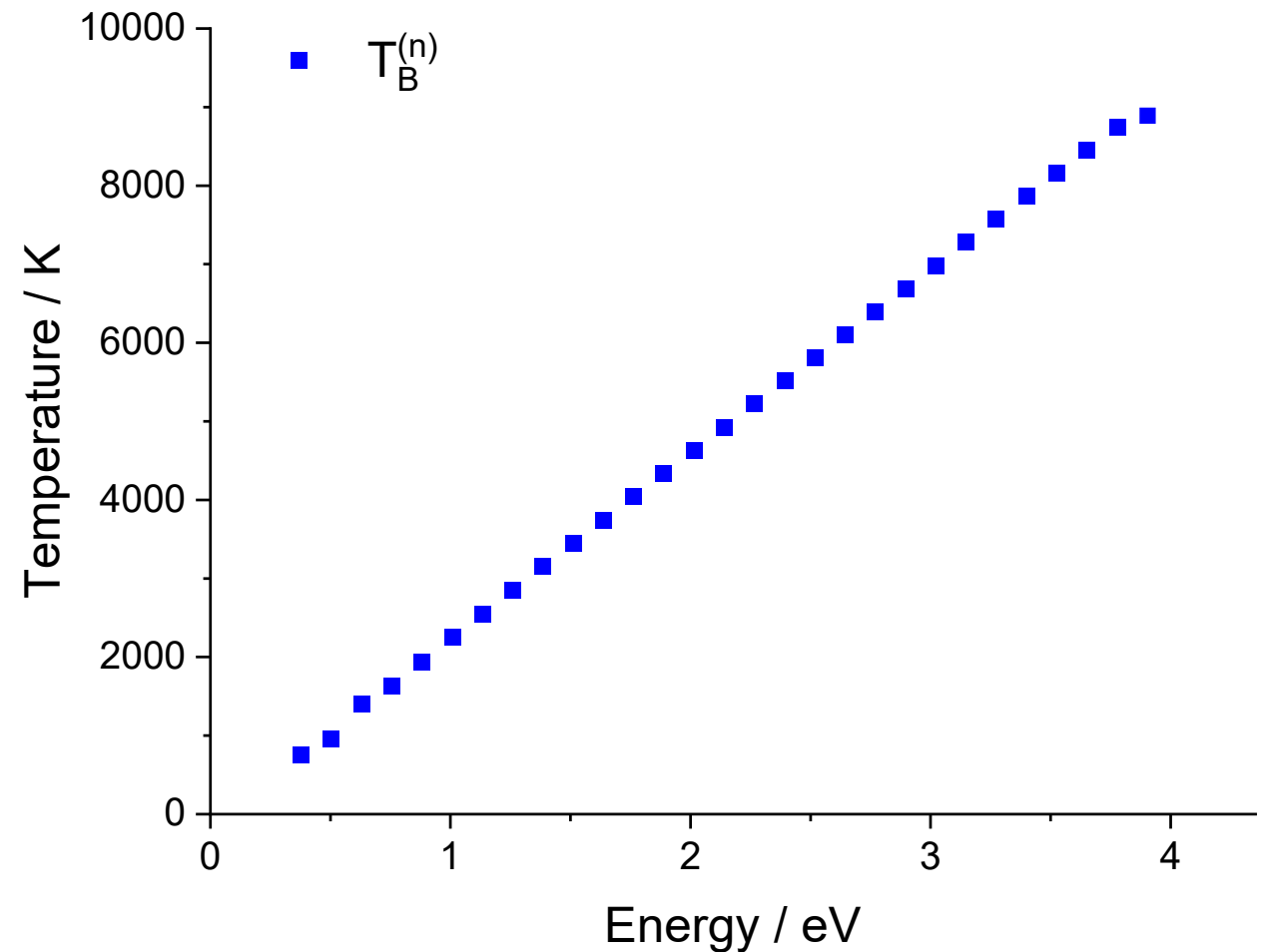
	$N = 3$					
	n_1	n_2	n_3	E	$\varepsilon\omega(E)$	$\Omega(E)$
$M = 0$	0	0	0	E_{ZP}	1	1
$M = 1$	1	0	0	$E_{ZP} + h\nu$		
	0	1	0	$E_{ZP} + h\nu$		
	0	0	1	$E_{ZP} + h\nu$	3	4
$M = 2$	1	1	0	$E_{ZP} + 2h\nu$		
	1	0	1	$E_{ZP} + 2h\nu$		
	0	1	1	$E_{ZP} + 2h\nu$		
	2	0	0	$E_{ZP} + 2h\nu$		
	0	2	0	$E_{ZP} + 2h\nu$		
	0	0	2	$E_{ZP} + 2h\nu$	6	10
$M = 3$	1	1	1	$E_{ZP} + 3h\nu$		
	:					
	0	0	3	$E_{ZP} + 3h\nu$	10	20

Boltzmann

$$\varepsilon\omega(E_M) = \left(\binom{N}{M} \right) = \binom{M+N-1}{M} \\ = \frac{(M+N-1)!}{(N-1)!M!}$$

$$S_B(E_M) = k_B \ln \left[\frac{(M+N-1)!}{(N-1)!M!} \right]$$

$$T_B^{(n)} = \left(\frac{\Delta S_B}{\Delta E} \right)^{-1}$$

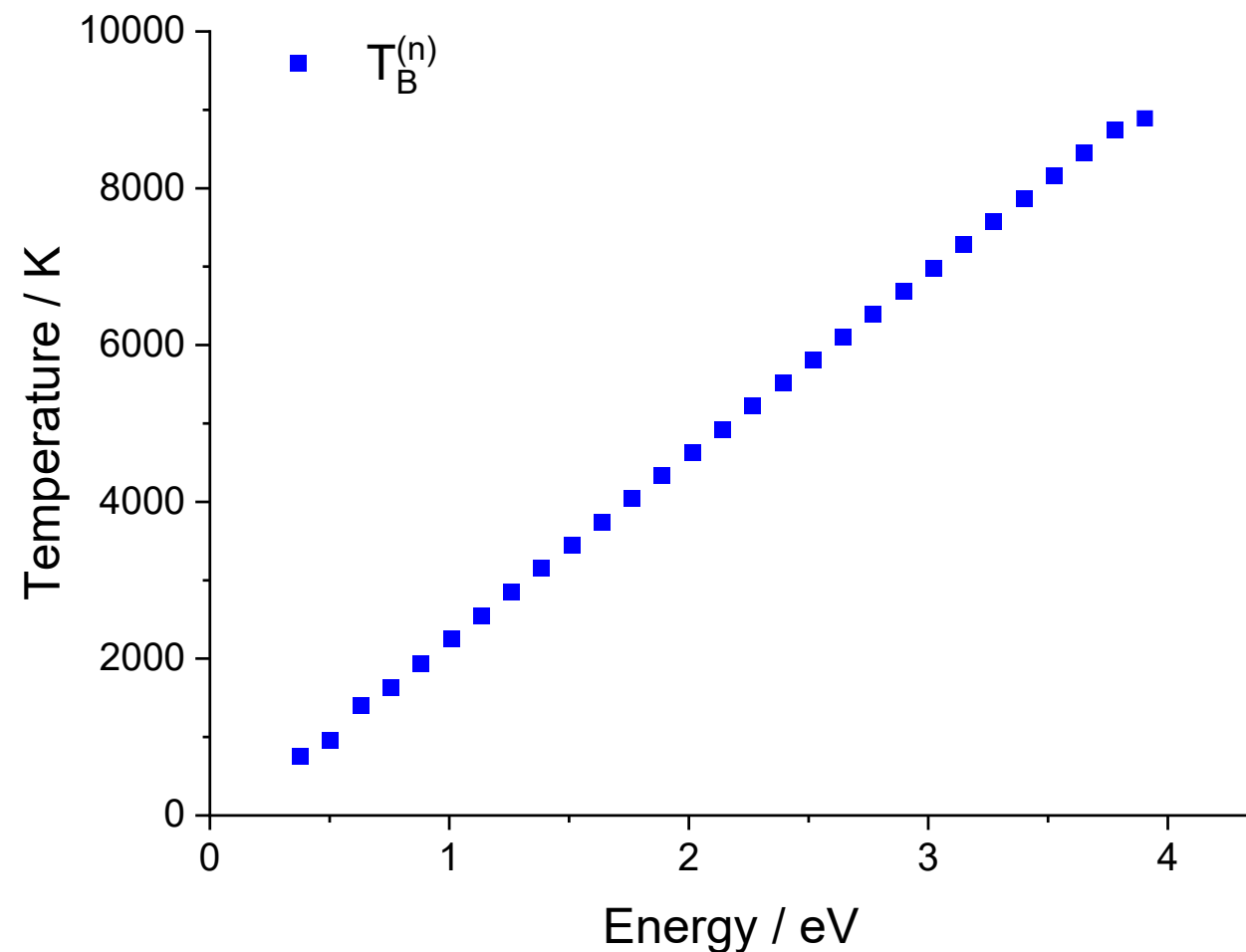


$$S_B(E_M) = k_B \ln \left[\frac{(M+N-1)!}{(N-1)!M!} \right]$$

Stirling's approximation

$$\ln(n!) \approx n \ln(n) - n$$

$$T_B^{(s)} = \left(\frac{\partial S_B}{\partial E} \right)^{-1} = \left(\ln \left[\frac{(2E + (N-2)h\bar{\nu})}{(2E - Nh\bar{\nu})} \right] \right)^{-1} \frac{h\bar{\nu}}{k_B}$$



$$S_B(E_M) = k_B \ln \left[\frac{(M+N-1)!}{(N-1)!M!} \right]$$

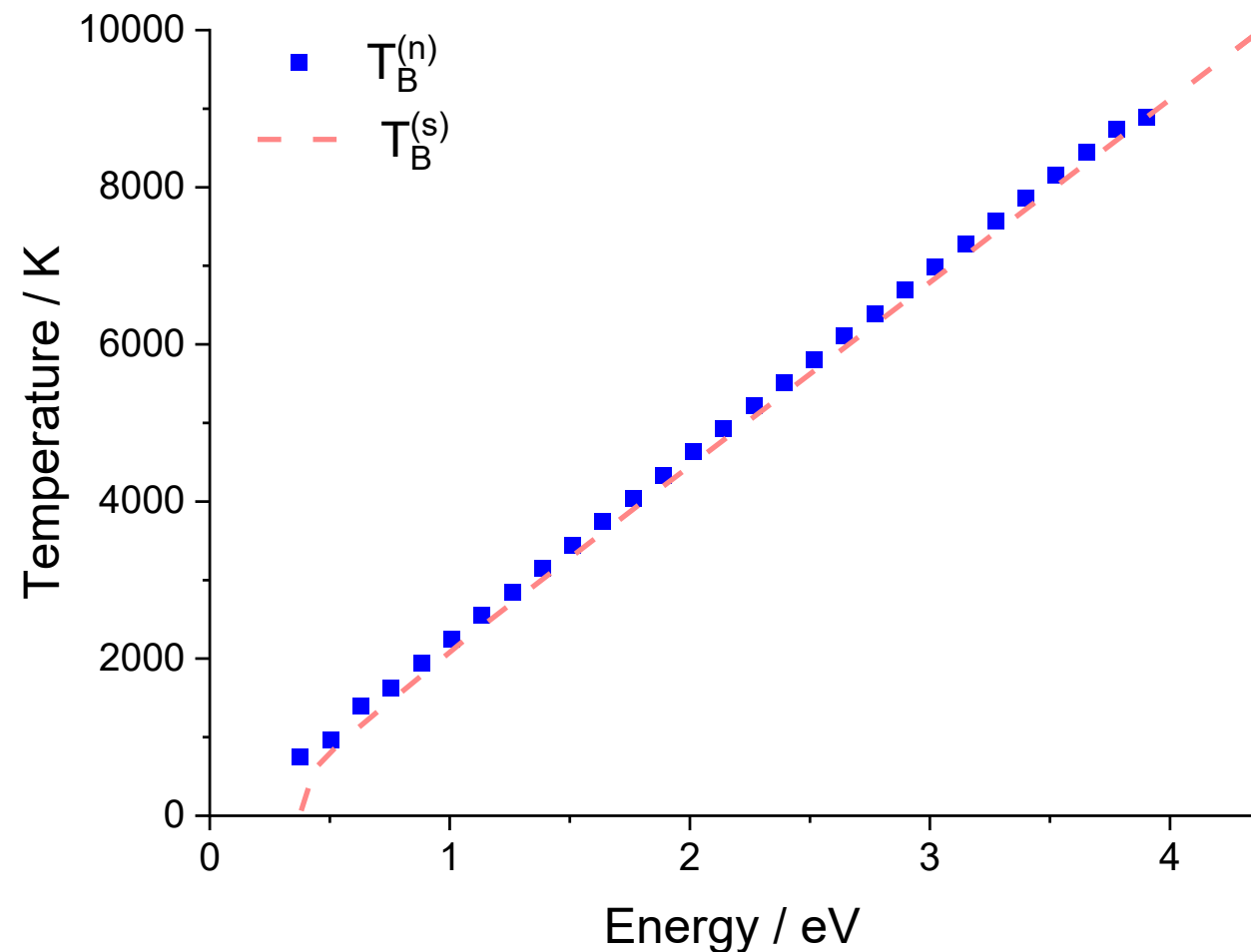
Stirling's approximation

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$N \gg 2$ approximation

$$T_B^{(l)} = \left(\ln \left[\frac{2E + Nh\bar{\nu}}{2E - Nh\bar{\nu}} \right] \right)^{-1} \frac{h\bar{\nu}}{k_B}$$



$$S_B(E_M) = k_B \ln \left[\frac{(M + N - 1)!}{(N - 1)! M!} \right]$$

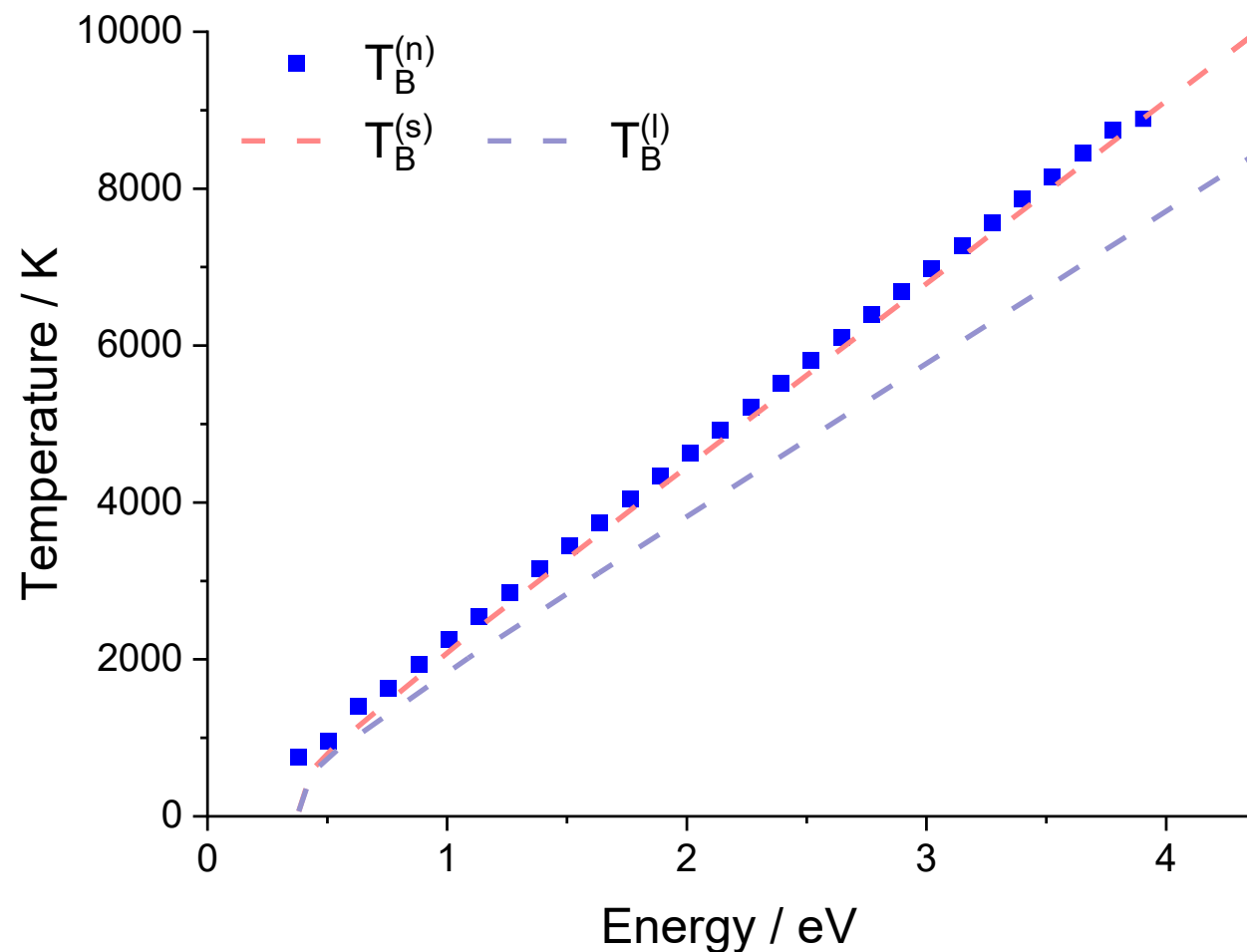
Stirling's approximation

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$N \gg 2$ approximation

$$T_B^{(l)} = \left(\ln \left[\frac{2E + Nh\bar{\nu}}{2E - Nh\bar{\nu}} \right] \right)^{-1} \frac{h\bar{\nu}}{k_B}$$

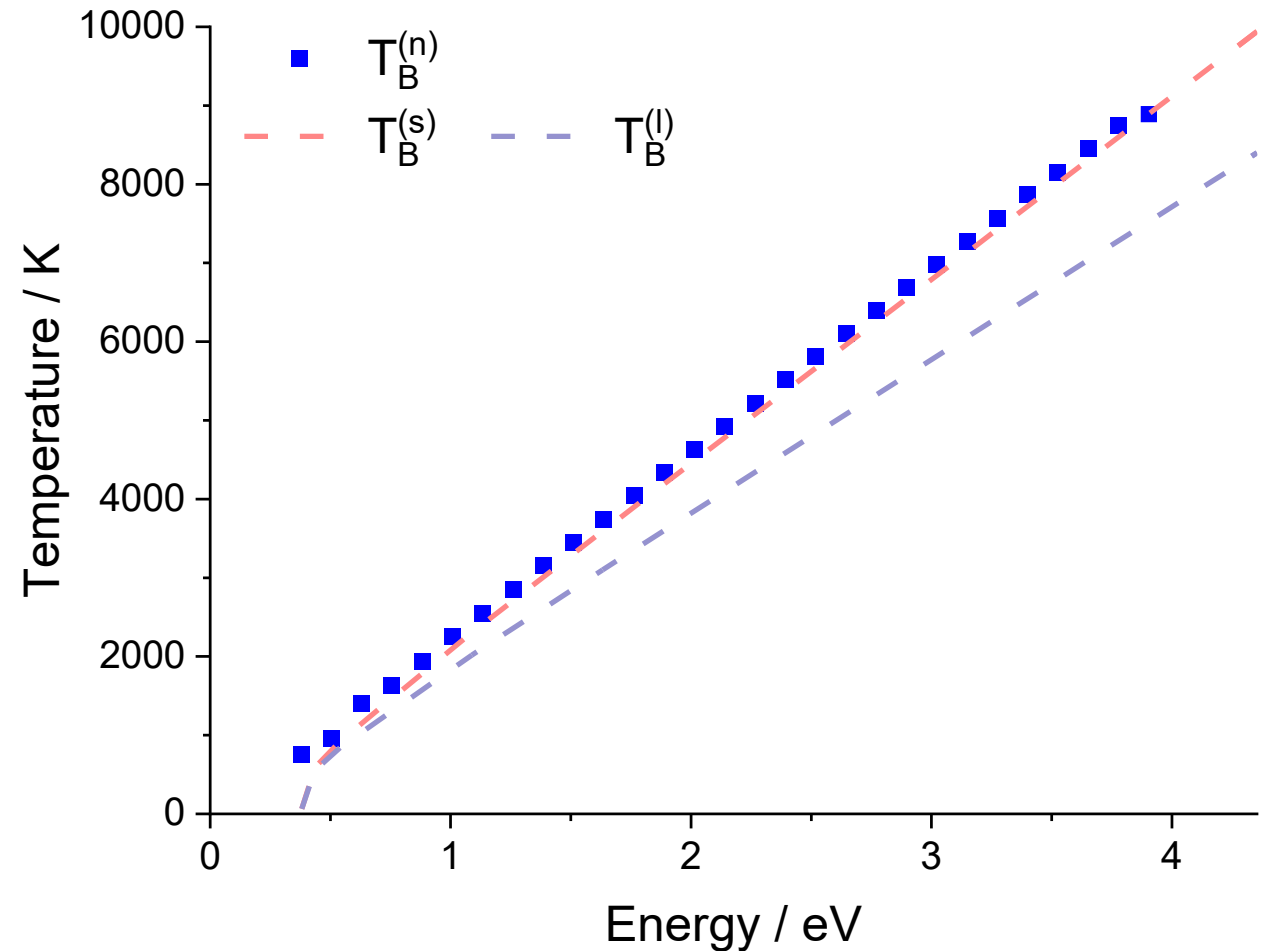


Gibbs volume

$$\Omega(E_M) = \sum_{K=0}^M \left(\binom{N}{K} \right) = \binom{M+N}{M} = \frac{(M+N)!}{N!M!}$$

Hockey-stick identity

$$\sum_{j=0}^{n-r} \binom{j+r}{r} = \binom{n+1}{n-r}$$



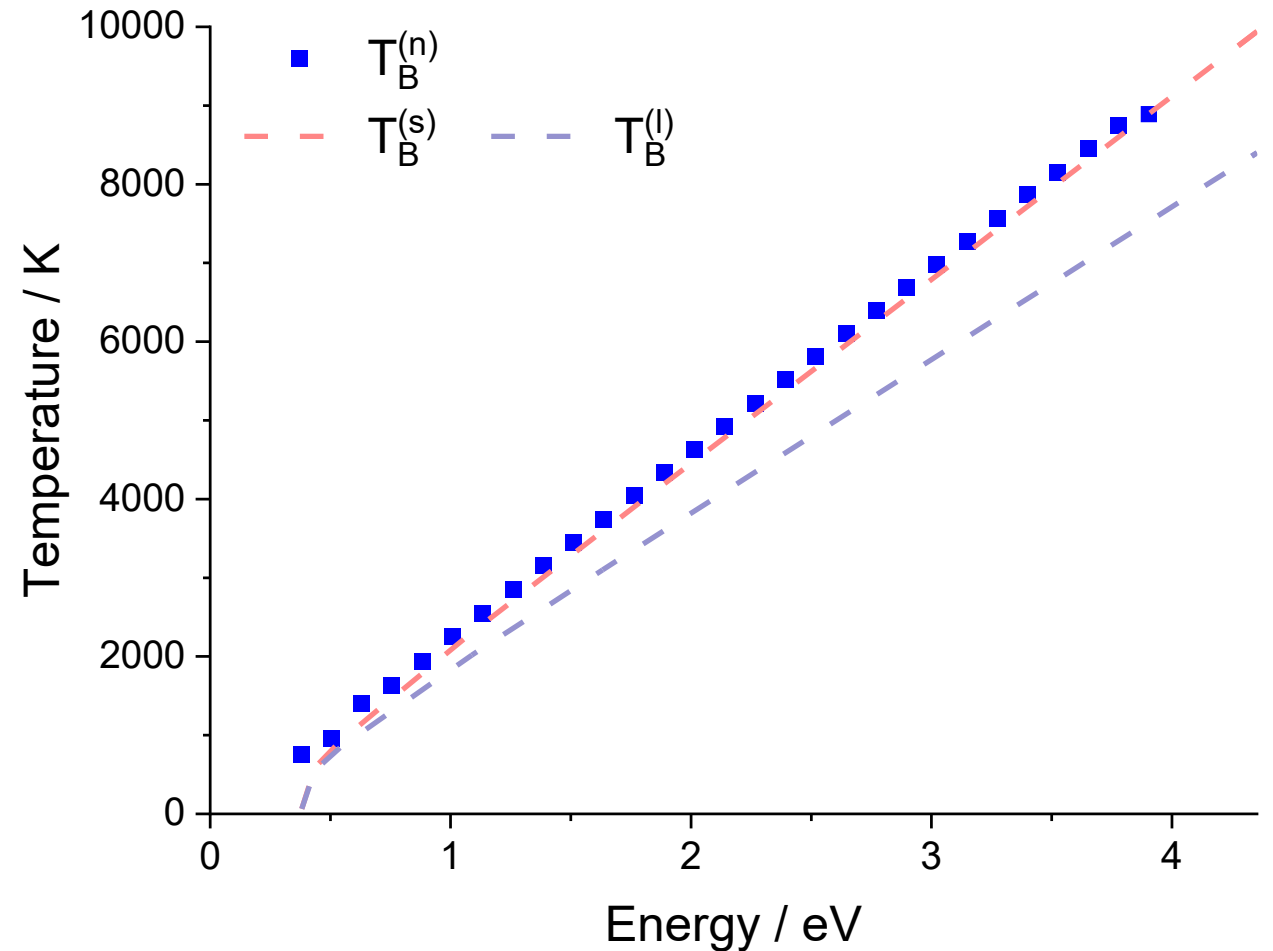
Hockey-stick identity: en.wikipedia.org/wiki/Hockey-stick_identity

Gibbs volume

$$\Omega(E_M) = \sum_{K=0}^M \left(\binom{N}{K} \right) = \binom{M+N}{M} = \frac{(M+N)!}{N!M!}$$

$$S_G(E_M) = k_B \ln \left[\frac{(M+N)!}{N!M!} \right]$$

$$T_G^{(n)} = \left(\frac{\Delta S_G}{\Delta E} \right)^{-1}$$

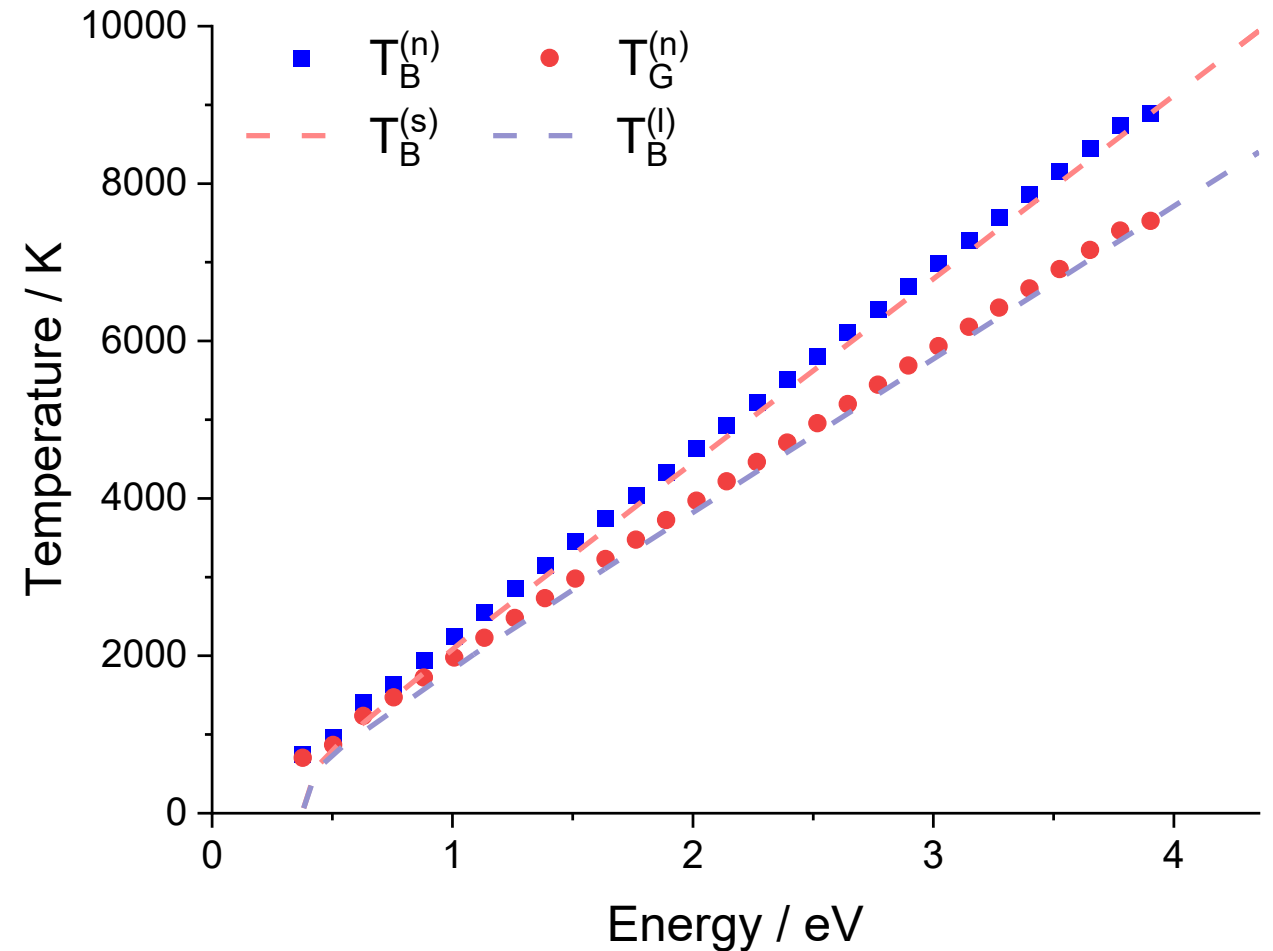


Gibbs volume

$$\Omega(E_M) = \sum_{K=0}^M \left(\binom{N}{K} \right) = \binom{M+N}{M} = \frac{(M+N)!}{N!M!}$$

$$S_G(E_M) = k_B \ln \left[\frac{(M+N)!}{N!M!} \right]$$

$$T_G^{(n)} = \left(\frac{\Delta S_G}{\Delta E} \right)^{-1}$$



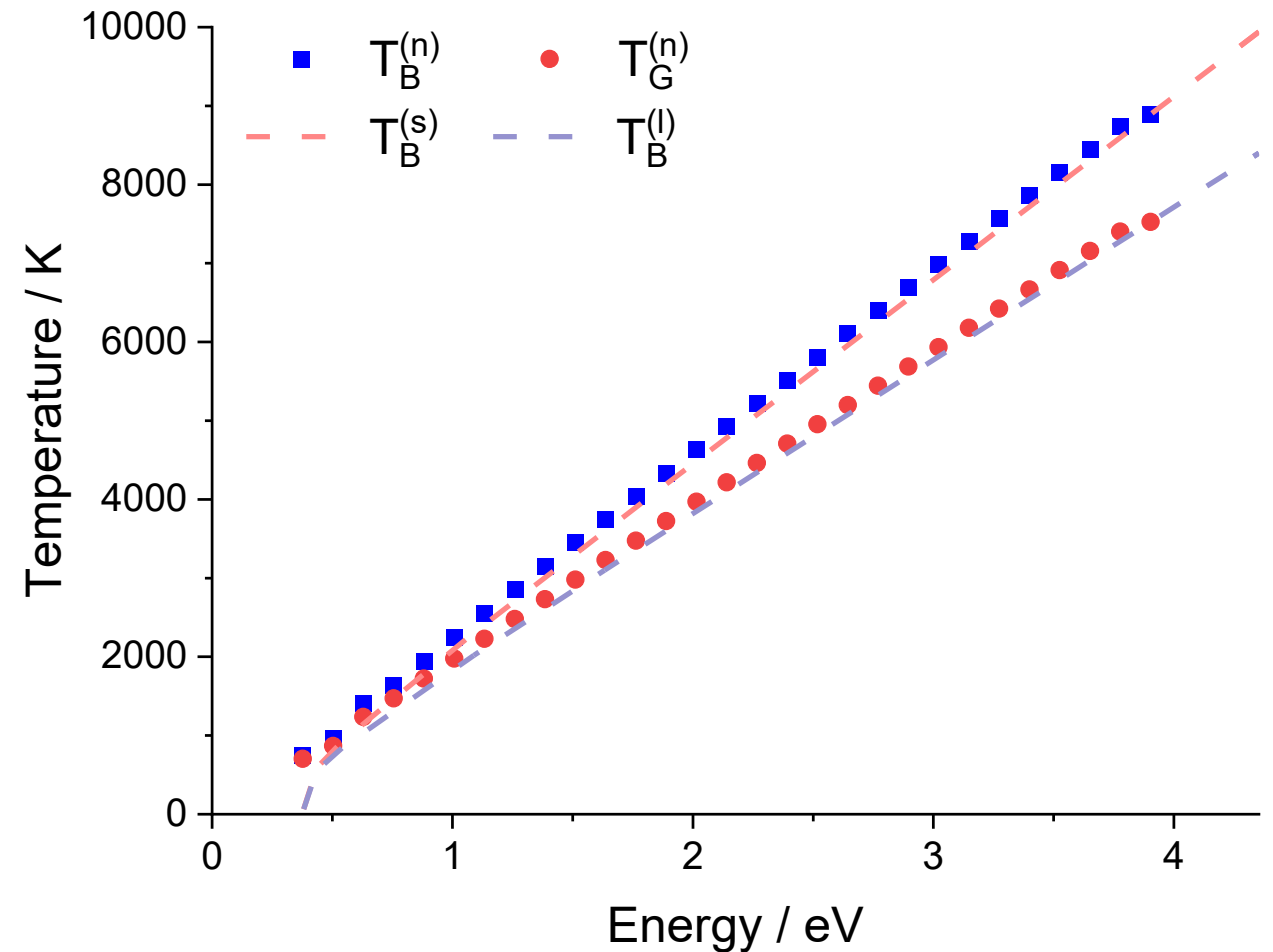
$$S_G(E_M) = k_B \ln \left[\frac{(M+N)!}{N!M!} \right]$$

$$T_G^{(n)} = \left(\frac{\Delta S_G}{\Delta E} \right)^{-1}$$

Stirling's approximation

$$T_G^{(s)} = \left(\frac{\partial S_G}{\partial E} \right)^{-1} = \left(\ln \left[\frac{2E + Nh\nu}{2E - Nh\nu} \right] \right)^{-1} \frac{h\nu}{k_B}$$

$$T_G^{(s)} = T_B^{(l)}$$



“*Large N* ” isn’t a simple numerical approximation.

It represents a shift from Boltzmann to
Gibbs volume formulation.



Back to the molecular problem

We want

$$\# \left\{ E_{\xi} = E_{ZP} + \sum_k n_k h\nu_k, \quad E_{\xi} \in [E, E + \varepsilon] \right\}$$

But we only know how to calculate

$$\# \left\{ E_M = E_{ZP} + Mh\bar{\nu}, \quad E_M \in [E, E + \varepsilon] \right\}$$

Equivalent degenerated model (EDM)

Given a molecule, there is an average frequency value in its spectrum that makes the degenerated-problem solution to be a good approximation for the non-degenerated problem.

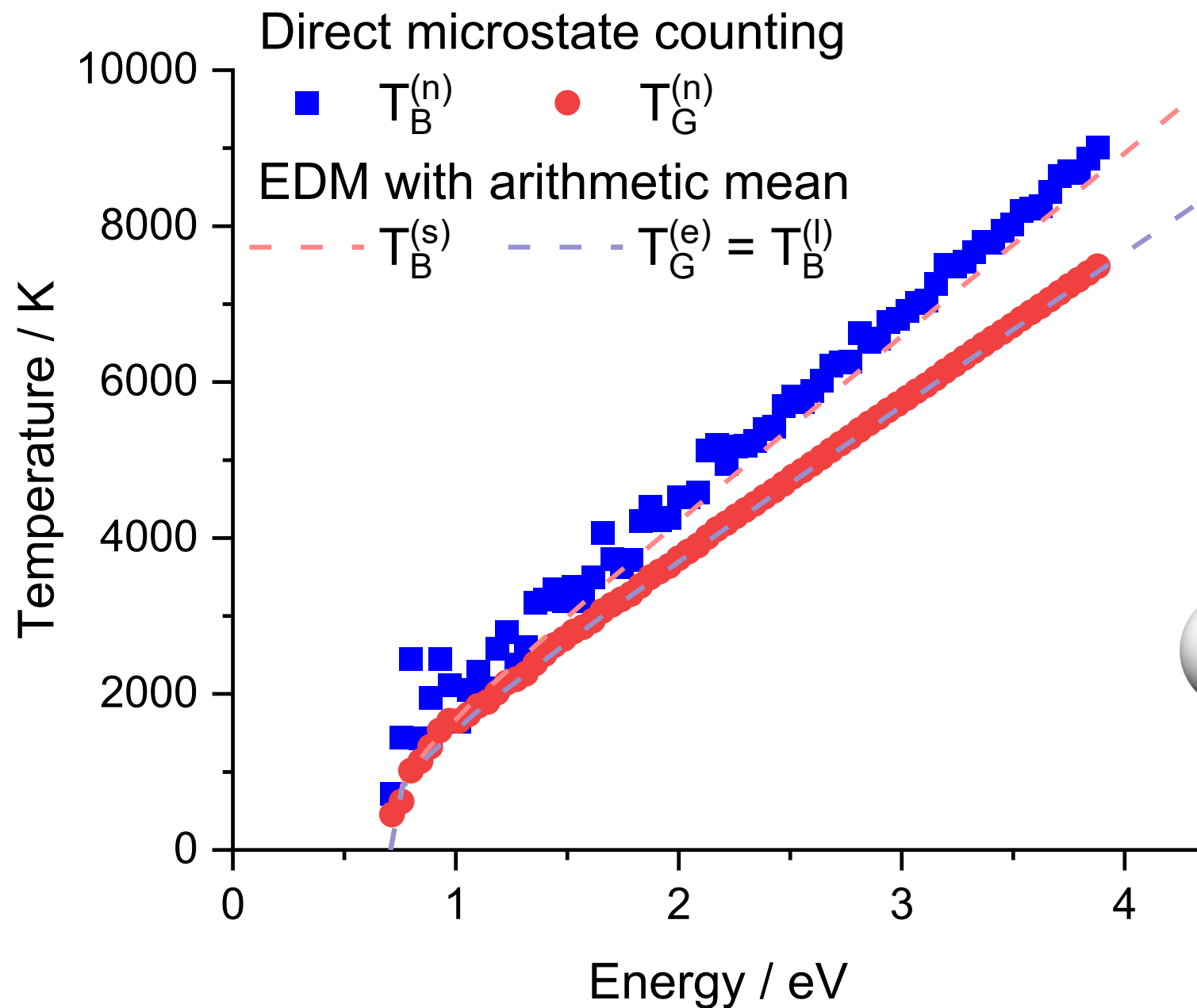
In the degenerated problem

$$T_G^{(s)} = T_B^{(l)} = \left(\ln \left[\frac{2E + Nh\bar{\nu}}{2E - Nh\bar{\nu}} \right] \right)^{-1} \frac{h\bar{\nu}}{k_B} \quad \text{and} \quad E_{ZP} = \frac{Nh\bar{\nu}}{2}$$

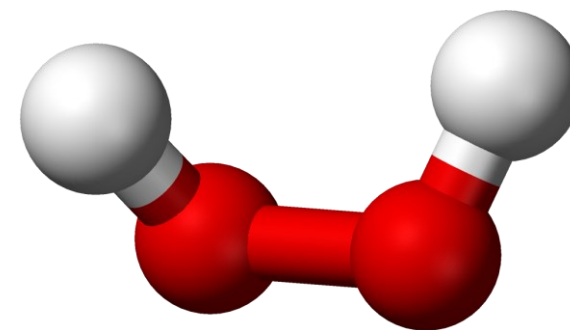
Therefore,

$$T_G^{(s)} = T_B^{(l)} = \left(\ln \left[\frac{E + E_{ZP}}{E - E_{ZP}} \right] \right)^{-1} \frac{2E_{ZP}}{Nk_B} \quad \text{and} \quad \bar{\nu} = \frac{2E_{ZP}}{N} = \frac{1}{N} \sum_k \nu_k$$

Thus, the **arithmetic mean** is a strong candidate to be tested.



$$\bar{\nu} = 1919 \text{ cm}^{-1}$$



Is the good agreement a coincidence?

Test set:

Non-degenerated models with N random frequencies
between 300 and 3000 cm^{-1}

- 10 models with $N = 6$
- 10 models with $N = 7$
- 10 models with $N = 8$

Evaluate the mean relative error

$$\delta T_{B/G} = \left| \frac{T_{B/G}^{(n)} - T_{B/G}^{(s)}(\bar{\nu})}{T_{B/G}^{(n)}} \right|$$

Mean relative error

	$N = 6$	$N = 7$	$N = 8$
$\langle \delta T_G \rangle$	0.03	0.03	0.03
$\langle \delta T_B \rangle$	0.08	0.08	0.08



Connection to previous approaches

Classical limit ($E_{kin} = Nk_B T / 2$)

$$T(E) \approx \frac{E}{Nk_B}$$

Andersen-Bonderup-Hansen model

$$T(E) \approx \frac{E}{(N-1)k_B}$$

Asymptotic expansion at $E \rightarrow \infty$

$$\begin{aligned} T_G^{(s)}(E) &= \left(\ln \left[\frac{2E + Nh\bar{\nu}}{2E - Nh\bar{\nu}} \right] \right)^{-1} \frac{h\bar{\nu}}{k_B} \\ &= \frac{E}{Nk_B} - \frac{Nh^2\bar{\nu}^2}{12k_BE} + O\left(\frac{1}{E^3}\right) \end{aligned}$$

$$\begin{aligned} T_B^{(s)}(E) &= \left(\ln \left[\frac{(2E + (N-2)h\bar{\nu})}{(2E - Nh\bar{\nu})} \right] \right)^{-1} \frac{h\bar{\nu}}{k_B} \\ &= \frac{E - \frac{1}{2}h\bar{\nu}}{(N-1)k_B} - \frac{(N-1)h^2\bar{\nu}^2}{12k_BE} + O\left(\frac{1}{E^2}\right) \end{aligned}$$

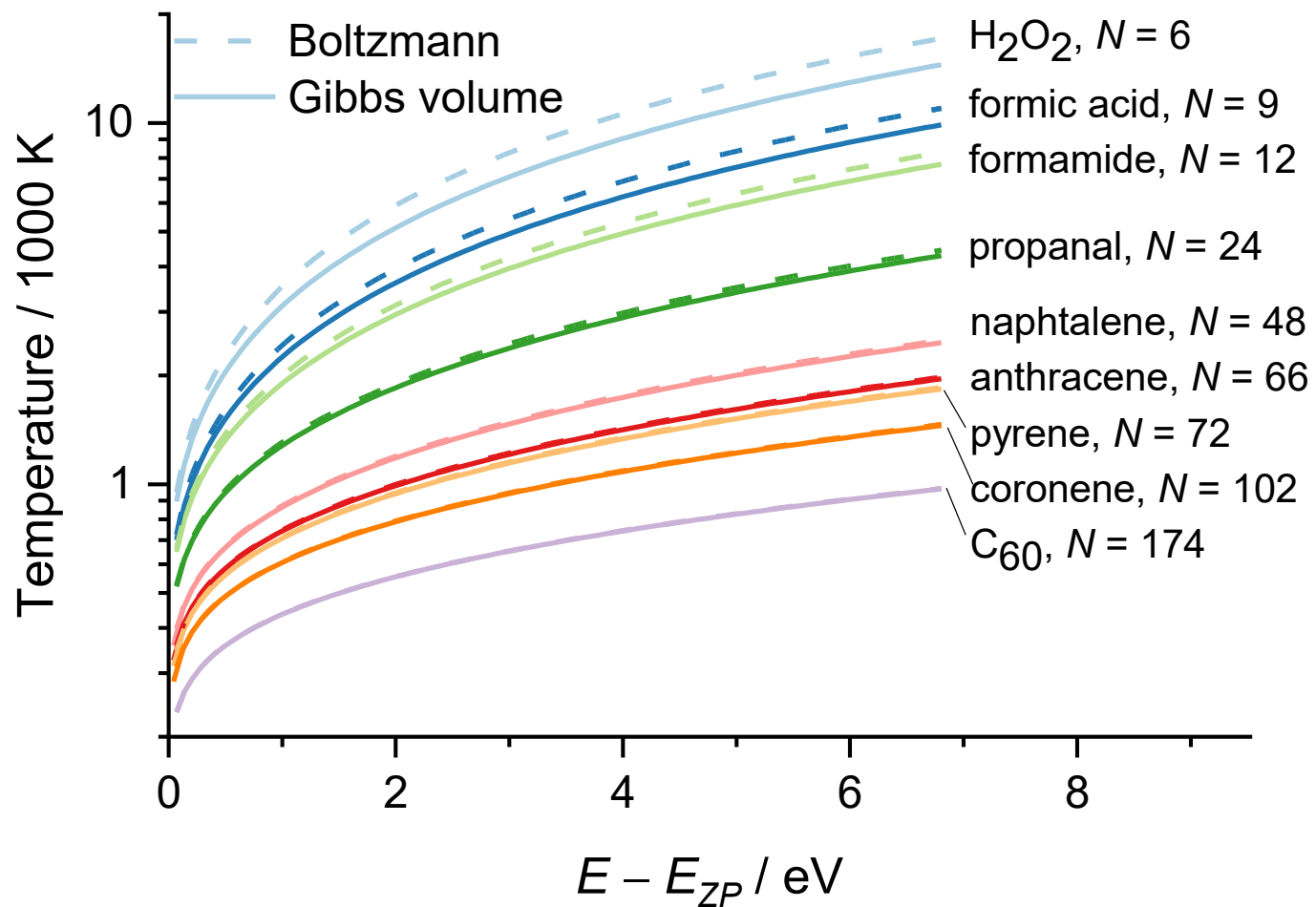
Linear approximation is valid only if

$$E \gg \frac{Nh\nu}{2\sqrt{3}} = \frac{E_{ZP}}{\sqrt{3}}$$

Even if the molecule is initially in the linear region, the radiative cooling brings it to the non-linear region.



The temperature of isolated molecules



Heat capacity of isolated C_{60} at 808 K

- Experimental: $12.6 \pm 1.4 \text{ meV/K}$

Deng; Echt. *J Phys Chem C* **2015**, 119, 11233

- Theory: 12.0 meV/K

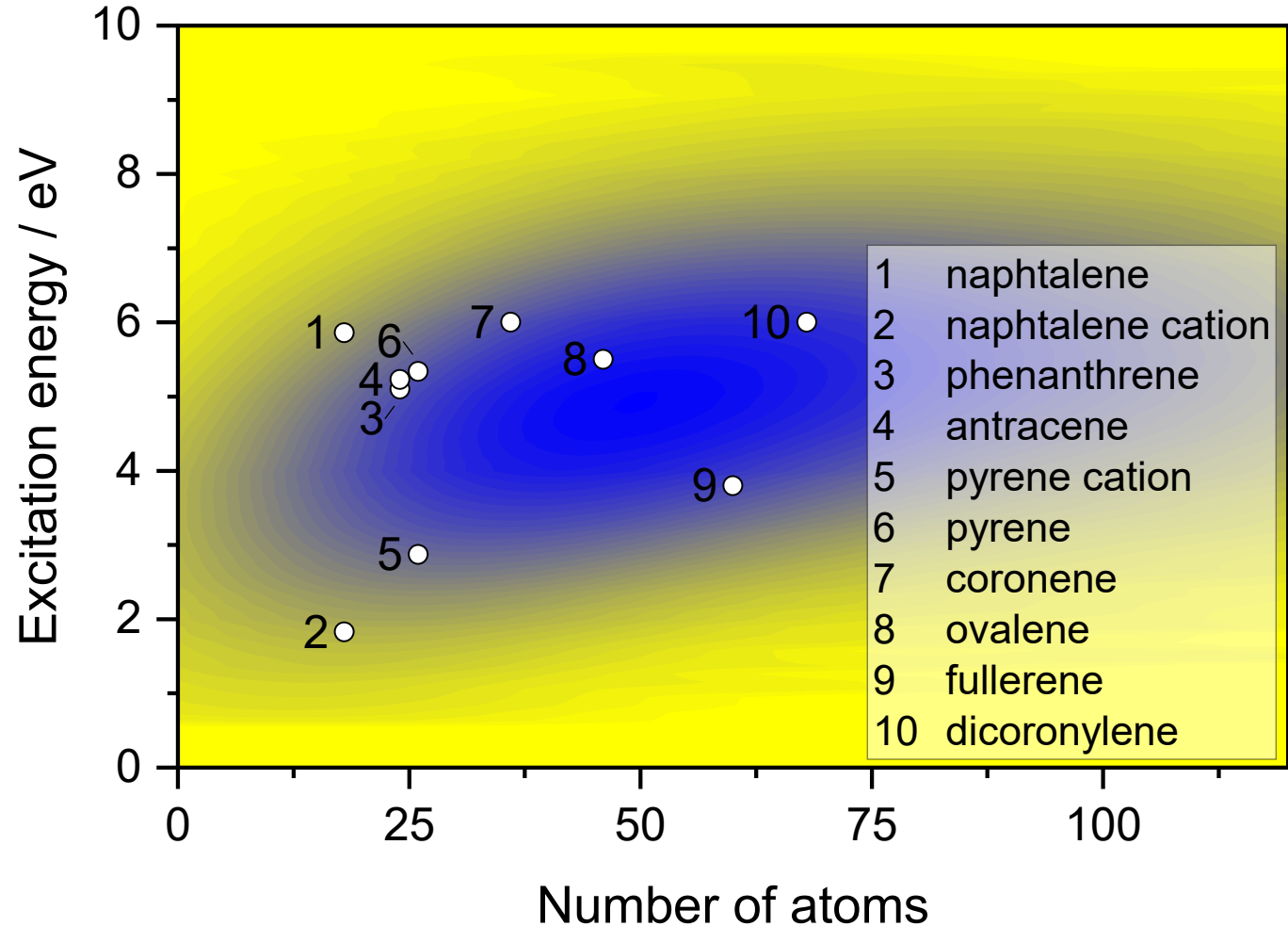
Interstellar PAH

1. Sample 10^6 random values for
 - peak temperature: 950 ± 150 K
 - mean frequency: 1100 ± 100 cm^{-1}
 - UV excitation: 5 ± 1 eV

2. Assume internal conversion to S_0

3. Solve T for N_{at}

$$N_{at} = \frac{\Delta E_{UV}}{3h\bar{\nu}} \left(\exp\left(\frac{h\bar{\nu}}{k_B T}\right) - 1 \right) + 2$$





Boltzmann or Gibbs volume,
which one is correct?



Thermodynamic laws in isolated systems

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²*Institute of Physics, University of Augsburg, Universitätsstraße 1, D-86135 Augsburg, Germany*

³*Nanosystems Initiative Munich, Schellingstr. 4, D-80799 München, Germany*

⁴*Department of Mathematics, Massachusetts Institute of Technology, 77 Massachusetts Avenue E17-412, Cambridge, Massachusetts 02139-4307, USA*

(Received 28 September 2014; published 9 December 2014)

The recent experimental realization of exotic matter states in isolated quantum systems and the ensuing controversy about the existence of negative absolute temperatures demand a careful analysis of the conceptual foundations underlying microcanonical thermostatistics. Here we provide a detailed comparison of the most commonly considered microcanonical entropy definitions, focusing specifically on whether they satisfy or violate the zeroth, first, and second laws of thermodynamics. Our analysis shows that, for a broad class of systems that includes all standard classical Hamiltonian systems, only the Gibbs volume entropy fulfills all three laws simultaneously. To avoid ambiguities, the discussion is restricted to exact results and analytically tractable examples.

PHYSICAL REVIEW E **92**, 020103(R) (2015)

Gibbs volume entropy is incorrect

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Jian-Sheng Wang[†]

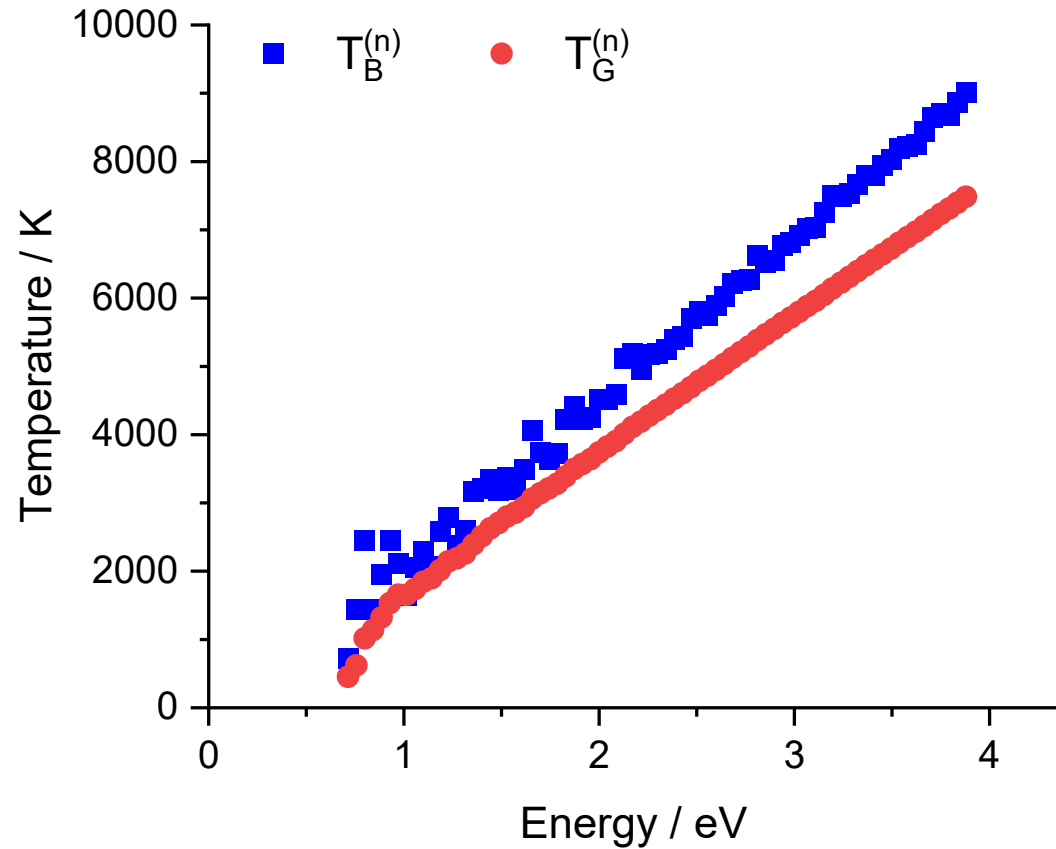
Department of Physics, National University of Singapore, Singapore 117551, Republic of Singapore

(Received 2 July 2015; published 21 August 2015)

We show that the expression for the equilibrium thermodynamic entropy contains an integral over a surface in phase space, and in so doing, we confirm that negative temperature is a valid thermodynamic concept. This demonstration disproves the claims of several recent papers that the Gibbs entropy, which contains an integral over a volume in phase space, is the correct definition and that thermodynamics cannot be extended to include negative temperatures. We further show that the Gibbs entropy fails to satisfy the postulates of thermodynamics and that its predictions for systems with nonmonotonic energy densities of states are incorrect.

Swendsen; Wang. *Phys Rev E* **2015**, 92, 020103

Review: Swendsen. *Rep Prog Phys* **2018**, 81, 072001



Recipe for checking which entropy is correct

1. Trap a 4-atoms ion in a electrostatic trap
2. Measure radiative cooling
3. Estimate the peak temperature
4. Compare to T_B and T_G



Conclusions

The microcanonical temperature of a isolated molecule within the *equivalent degenerated model approximation* is

$$T_G^{(s)} = T_B^{(l)} = \left[\ln \left(\frac{E + E_{ZP}}{E - E_{ZP}} \right) \right]^{-1} \frac{2E_{ZP}}{Nk_B}$$

This expression allows estimating the molecular temperature within $\pm 3\%$ for a harmonic molecule with more than 10 atoms.

For smaller molecules, the difference between temperatures predicted with Boltzmann and Gibbs volume entropies is significant.

This difference may be experimentally verified.

The theory should be generalized to anharmonic effects.





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tinyurl.com/preprint-b22-1