Partition Functions

Energy levels are quantized → How are the various energy levels populated at a given temperature?

Boltzmann Equation

$$p_j \propto e^{-E_j/kT}$$

p_j is the probability that the system is in a level with energy E_j; k is the Boltzmann constant, and T is the temperature.

The sum of the probabilities should be normalized:

$$\sum_j p_j = 1$$

The normalization constant

$$Q = \sum_j e^{-E_j/kT}$$

is called the **Partition function**.

Consider a system of volume V with N particles. The Schrödinger equation for the N-body system is

$$\hat{H}_N \psi_j = E_j \psi_j \qquad j = 1, 2, \ldots$$

For an ideal gas, i.e. N non-interacting particles,

$$E_j(N, V) = \varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_N$$

is the sum of their individual energies. For example, a monoatomic ideal gas in a cube of side a has translational energy

$$\varepsilon_{n_x, n_y, n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \qquad a = V^{1/3}$$

Thus $E_j(N,V)$ depends on N through the number of terms only. The equations given below apply to the general N-particle system.

To determine whether the system is in a particular state j with energy $E_j(N,V)$, we need to consider a very large number of systems in contact with an infinite heat reservoir at temperature T.

Each system has the same values of N, V, $T \rightarrow$ **ensemble** (but the N particles are organized into different distributions, or systems, called "microstates").

We now look for the relative number of systems of the ensemble that would be found in each state. Consider two states 1, 2 with energies $E_1(N,V)$ and $E_2(N,V)$. We can write

$$\frac{a_2}{a_1} = f(E_1, E_2)$$

a_2 = number of systems in the ensemble that have energy E_2; a_1 = number of systems that have energy E_1.

$f(E_1, E_2) \rightarrow f(E_1 - E_2)$, since it is related to the relative difference in energy. Thus,

$$\frac{a_2}{a_1} = f(E_1 - E_2)$$

This must be true for any other pair of energy states:

$$\frac{a_3}{a_2} = f(E_2 - E_3), \qquad \frac{a_3}{a_1} = f(E_1 - E_3)$$

Note

$$\frac{a_3}{a_1} = \frac{a_2}{a_1} \cdot \frac{a_3}{a_2}$$

Thus, the function must satisfy

$$f(E_1 - E_3) = f(E_1 - E_2)\, f(E_2 - E_3)$$

$\rightarrow$ the function $f(E)$ has the form $e^{\beta E}$:

$$\frac{a_2}{a_1} = e^{\beta(E_1 - E_2)}$$

In general,

$$\frac{a_n}{a_m} = e^{\beta(E_m - E_n)} \qquad \text{thus,} \quad a_j = C\, e^{-\beta E_j}$$

C is a normalization constant. Now, $\Sigma a_j = A$, the total number of systems in the ensemble. Thus,

$$C = \frac{\sum_j a_j}{\sum_j e^{-\beta E_j}} = \frac{A}{\sum_j e^{-\beta E_j}} \qquad \frac{a_j}{A} = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

a_j/A is the fraction of systems in the ensemble that are found in state j with energy $E_j \rightarrow$ the probability of the system being in state j:

$$p_j = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

The quantity

$$Q(N, V, \beta) = \sum_i e^{-\beta E_i(N, V)}$$

Thus,

$$p_j(N, V, \beta) = \frac{e^{-\beta E_j(N, V)}}{\sum_i e^{-\beta E_i(N, V)}} = \frac{e^{-\beta E_j(N, V)}}{Q}$$

The factor $\beta = 1/kT$, where k is the Boltzmann constant.

Average Energy

$$\langle E \rangle = \sum_j p_j(N, V, \beta)\, E_j(N, V) = \sum_j \frac{E_j(N, V)\, e^{-\beta E_j(N, V)}}{Q(N, V, \beta)}$$

<E> is a function of N, V, β. It should be possible to express <E> in terms of the partition function.

$$\left(\frac{\partial \ln Q(N,V,\beta)}{\partial \beta}\right)_{N,V} = \frac{1}{Q(N,V,\beta)}\left(\frac{\partial \sum_j e^{-\beta E_j(N,V)}}{\partial \beta}\right)_{N,V}$$

$$= \frac{1}{Q(N,V,\beta)}\sum_j -E_j(N,V)\, e^{-\beta E_j(N,V)} = -\sum_j \frac{E_j(N,V)\, e^{-\beta E_j(N,V)}}{Q(N,V,\beta)} = -\langle E\rangle$$

Thus,

$$\langle E\rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$$

Remembering β = 1/kT,

$$\langle E\rangle = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

It will be shown later that for an ideal monoatomic gas

$$Q(N,V,\beta) = \frac{q(V,\beta)^N}{N!} \qquad q(V,\beta) = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V$$

$$\ln Q = N\ln q - \ln N!$$

$$= -\frac{3N}{2}\ln\beta + \frac{3N}{2}\ln\left(\frac{2\pi m}{h^2}\right) + N\ln V - \ln N!$$

The last three terms are terms in N and V only.

$$\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = -\frac{3N}{2}\frac{d\ln\beta}{d\beta} = -\frac{3N}{2\beta} = -\frac{3}{2}NkT$$

$$\langle E\rangle = \frac{3}{2}NkT$$

When $N = nN_A$ ($N_A \rightarrow$ Avogadro's number),

$$\langle E \rangle = \frac{3}{2} nRT \qquad \text{where } R = kN_A \longrightarrow \text{universal gas constant}$$

This is the same result obtained from the kinetic theory of gases. Per mole,

$$\bar{U} = \langle E \rangle = \frac{3}{2} RT = \frac{1}{2} RT + \frac{1}{2} RT + \frac{1}{2} RT$$

one ½RT for each of the 3 translational degrees of freedom.

Constant Volume Heat Capacity

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

$$C_V = \frac{3}{2} R$$

Average Pressure

The average pressure of the system is given by

$$\langle P \rangle = \sum_j p_j(N,V,\beta)\, P_j(N,V) = \sum_j p_j(N,V,\beta) \left(-\frac{\partial E_j}{\partial V} \right)_N$$

$$= \sum_j \left(-\frac{\partial E_j}{\partial V} \right)_N \frac{e^{-\beta E_j(N,V)}}{Q(N,V,\beta)}$$

Note: $P_j(N,V) = -(\partial E_j / \partial V)_N$

Start with the partition function and differentiate with respect to V, keeping N, β constant:

$$Q(N,V,\beta) = \sum_j e^{-\beta E_j(N,V)}$$

$$\left(\frac{\partial Q}{\partial V} \right)_{N,\beta} = -\beta \sum_j \left(\frac{\partial E_j}{\partial V} \right)_N e^{-\beta E_j(N,V)}$$

Remembering the expression for <P> above, note

$$\langle P\rangle = \frac{kT}{Q(N,V,\beta)}\left(\frac{\partial Q}{\partial V}\right)_{N,\beta} \qquad or \qquad \langle P\rangle = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

Recall, for an ideal monoatomic gas,

$$\ln Q = N\ln q - \ln N! \qquad q(V,\beta) = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V$$

$$\ln Q = \frac{3N}{2}\ln\left(\frac{2\pi m}{h^2\beta}\right) + N\ln V - \ln N!$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{N}{V} \qquad \langle P\rangle = \frac{NkT}{V}$$

In Summary

The partition function of a system is given by

$$Q = \sum_i e^{-\beta E_i(N,V)}$$

Physical quantities may be expressed in terms of the partition function:

$$\langle E\rangle = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} \qquad \langle P\rangle = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

Molecular Partition Functions

Consider a system of N distinguishable particles, with individual particle energies ε_j^{α}. The total energy of the system is given by

$$E_j(N,V) = \varepsilon_k^a(V) + \varepsilon_l^b(V) + \cdots$$

The superscript labels the particle (a, b, …) and the subscript labels its energy state.

$$Q(N,V,T) = \sum_j e^{-\beta E_j} = \sum_{k,l} e^{-\beta(\varepsilon_k^a + \varepsilon_l^b + \cdots)}$$

Since the particles are distinguishable and independent,

$$Q(N,V,T) = \sum_k e^{-\beta\varepsilon_k^a} \sum_l e^{-\beta\varepsilon_l^b} \cdots = q_a(V,T)\, q_b(V,T)\, q_c(V,T) \cdots$$

where

$$q(V,T) = \sum_i e^{-\beta\varepsilon_i}$$

Thus,

$$Q(N,V,T) = [q(V,T)]^N$$

For a system of N indistinguishable particles,

$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!}$$

Remember

$$\langle E \rangle = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V = N \sum_j \frac{\varepsilon_j e^{-\varepsilon_j/kT}}{q(V,T)}$$

For N independent particles,

$$\langle E \rangle = N\langle \varepsilon \rangle \qquad \langle \varepsilon \rangle = \sum_j \varepsilon_j \frac{e^{-\varepsilon_j/kT}}{q(V,T)}$$

$$\pi_j = \frac{e^{-\varepsilon_j/kT}}{q(V,T)}$$

is the probability that a molecule is in its j^{th} energy state.

This situation can be further simplified:

$$\varepsilon = \varepsilon_i^{trans} + \varepsilon_j^{rot} + \varepsilon_k^{vib} + \varepsilon_l^{elec}$$

Using similar reasoning, we can write

$$q(V,T) = q_{trans}\, q_{rot}\, q_{vib}\, q_{elec}$$

The individual partition functions are multiplicative. Summing over states,

$$q(V,T) = \sum_{j\ (states)} e^{-\varepsilon_j/kT}$$

In the case of degenerate systems, several states have the same energy. In the case of summation over energies,

$$q(V,T) = \sum_{j\ (energies)} g_j\, e^{-\varepsilon_j/kT}$$

e.g. for a rigid rotator,

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \qquad g_J = 2J+1$$

$$q_{rot} = \sum_{J=0}^{\infty} (2J+1)\, e^{-\hbar^2 J(J+1)/2IkT}$$

Problems

Data: $k = 1.381 \times 10^{-23}\ J\ K^{-1}$ $R = 8.314\ J\ K^{-1}\ mol^{-1}$

$h = 6.626 \times 10^{-34}\ J\ s$ $\hbar = 1.055 \times 10^{-34}\ J\ s$

Problem 1

The partition function for an atomic crystal of N atoms in the Einstein model is given by

$$Q = e^{-\beta U_0}\left(\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}\right)^{3N}$$

$U_0 \rightarrow$ sublimation energy at 0 K

Calculate the molar heat capacity. What is the high-temperature limit of the molar heat capacity?

Solution

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$$

$$= -\frac{\partial}{\partial \beta}\left[-\beta U_0 - \frac{3N}{2}\beta h\nu - 3N\ln(1-e^{-\beta h\nu})\right]_{N,V}$$

$$= U_0 + \frac{3Nh\nu}{2} + \frac{3Nh\nu e^{-\beta h\nu}}{1-e^{-\beta h\nu}}$$

U_0: sublimation energy; $3N\hbar\omega/2$: zero-point energy; the last term represents the β-dependence of U.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = -\frac{1}{kT^2}\left(\frac{\partial U}{\partial \beta}\right)_{N,V}$$

$$= -\frac{3Nh\nu}{kT^2}\left[-\frac{h\nu e^{-\beta h\nu}}{1-e^{-\beta h\nu}} - \frac{h\nu e^{-2\beta h\nu}}{(1-e^{-\beta h\nu})^2}\right]$$

$$= -\frac{3Nh\nu}{kT^2}\left[\frac{-h\nu e^{-\beta h\nu}(1-e^{-\beta h\nu}) - h\nu e^{-2\beta h\nu}}{(1-e^{-\beta h\nu})^2}\right]$$

$$= \frac{3Nh\nu}{kT^2}\cdot\frac{h\nu e^{-\beta h\nu}}{(1-e^{-\beta h\nu})^2} = \frac{3Nh\nu}{kT^2}\cdot\frac{h\nu e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2}$$

$$= 3Nk\left(\frac{h\nu}{kT}\right)^2\frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2}$$

When $N = N_A$,

$$C_V = 3R\left(\frac{h\nu}{kT}\right)^2\frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2}$$

At high temperature, $h\nu/kT << 1$. Since $e^x = 1 + x + x^2/2! + x^3/3! + \ldots$,

$$e^{-h\nu/kT} = 1 - \frac{h\nu}{kT} + \cdots \approx 1 - \frac{h\nu}{kT}$$

$$1 - e^{-h\nu/kT} \approx \frac{h\nu}{kT} \qquad e^{-h\nu/kT} \approx 1$$

$$C_V = 3R\left(\frac{h\nu}{kT}\right)^2 \times \frac{1}{(h\nu/kT)^2} = 3R$$

Problem 2

Calculate the equation of state associated with the partition function

$$Q(N,V,\beta) = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2}(V-Nb)^N e^{\beta aN^2/V}$$

Solution

Note:

$$\langle P\rangle = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

$$\ln Q = N\ln(V - Nb) + \frac{\beta a N^2}{V} + \text{terms that do not depend on } V$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{N}{V - Nb} - \frac{\beta a N^2}{V^2}$$

$$kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

For $N = N_A$, $Nk = R$:

$$P = \frac{RT}{V - Nb} - \frac{aN^2}{V^2}$$

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = RT$$

Van der Waals equation

Problem 3

A molecule has two non-degenerate energy levels, $\varepsilon_0 = 0$ and $\varepsilon_1 = \varepsilon$.

(a) Write down the molecular partition function q and the probability of finding the molecule in each level.

(b) Using $\langle\varepsilon\rangle = -(\partial \ln q/\partial\beta)$, show that $\langle\varepsilon\rangle = \varepsilon/(e^{\beta\varepsilon} + 1)$.

(c) What are the limits of $\langle\varepsilon\rangle$ as $T \to 0$ and $T \to \infty$? Explain.

(d) For $\varepsilon = 4.00 \times 10^{-21}$ J, calculate the fraction of molecules in the upper level and $\langle\varepsilon\rangle$ at 298 K.

Solution

(a)

$$q = \sum_j e^{-\beta\varepsilon_j} = e^0 + e^{-\beta\varepsilon} = 1 + e^{-\beta\varepsilon}$$

$$\pi_0 = \frac{1}{1+e^{-\beta\varepsilon}} \qquad \pi_1 = \frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}$$

(b)

$$\langle\varepsilon\rangle = -\left(\frac{\partial \ln q}{\partial\beta}\right) = -\frac{1}{q}\frac{\partial q}{\partial\beta} = \frac{\varepsilon e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}$$

Multiplying top and bottom by $e^{\beta\varepsilon}$,

$$\langle\varepsilon\rangle = \frac{\varepsilon}{e^{\beta\varepsilon}+1}$$

Check: $\langle\varepsilon\rangle = \Sigma\, \varepsilon_j\pi_j = (0)\pi_0 + \varepsilon\pi_1$, the same result.

(c) $T \to 0$: $\beta \to \infty$, so $e^{\beta\varepsilon} \to \infty$ and $\langle\varepsilon\rangle \to 0$. All molecules are in the lower level.

$T \to \infty$: $\beta \to 0$, so $e^{\beta\varepsilon} \to 1$ and $\langle\varepsilon\rangle \to \varepsilon/2$. Both levels are equally populated ($\pi_0 = \pi_1 = ½$); the upper level can never hold more than half the molecules at thermal equilibrium.

(d)

$$\beta\varepsilon = \frac{\varepsilon}{kT} = \frac{4.00\times10^{-21}}{(1.381\times10^{-23})(298)} = \frac{4.00\times10^{-21}}{4.115\times10^{-21}} = 0.972$$

$$e^{-0.972} = 0.378 \qquad \pi_1 = \frac{0.378}{1.378} = 0.274$$

$$\langle\varepsilon\rangle = \varepsilon\,\pi_1 = (4.00\times10^{-21}\ \text{J})(0.274) = 1.10\times10^{-21}\ \text{J}$$

Problem 4

For a rigid rotator, $\varepsilon_J = \hbar^2 J(J+1)/2I$ with degeneracy $g_J = 2J+1$. For HCl, $I = 2.644\times10^{-47}$ kg m^2.

(a) Calculate $\hbar^2/2I$. Calculate the ratio of the number of molecules in level J to that in level $J = 0$, n_J/n_0, for $J = 1$, 2, 3 and 4 at 298 K. Which level is the most populated?

(b) At high temperature the sum in q_{rot} may be replaced by an integral. Show that $q_{rot} \approx 2IkT/\hbar^2$, and evaluate it for HCl at 298 K.

(c) Using $\langle E \rangle = NkT^2(\partial \ln q/\partial T)_V$, show that the rotational contribution to the molar energy is RT and to the molar heat capacity is R.

Solution

(a)

$$\frac{\hbar^2}{2I} = \frac{(1.055\times10^{-34})^2}{2(2.644\times10^{-47})} = 2.105\times10^{-22}\ \text{J}$$

$$\frac{\hbar^2}{2IkT} = \frac{2.105\times10^{-22}}{4.115\times10^{-21}} = 0.0511$$

The population of level J is proportional to its degeneracy times its Boltzmann factor, so

$$\frac{n_J}{n_0} = (2J+1)\,e^{-\hbar^2 J(J+1)/2IkT} = (2J+1)\,e^{-0.0511\,J(J+1)}$$

$J=1$: $3e^{-0.102} = 2.71$ $\quad$ $J=2$: $5e^{-0.307} = 3.68$

$J=3$: $7e^{-0.614} = 3.79$ $\quad$ $J=4$: $9e^{-1.023} = 3.24$

$J = 3$ is the most populated level. The degeneracy $2J + 1$ increases with J while the Boltzmann factor decreases, so the population passes through a maximum.

(b) Let $x = J(J + 1)$, so $dx = (2J + 1)dJ$:

$$q_{rot} \approx \int_0^\infty (2J+1)\,e^{-\hbar^2 J(J+1)/2IkT}\,dJ = \int_0^\infty e^{-\hbar^2 x/2IkT}\,dx = \frac{2IkT}{\hbar^2}$$

$$q_{rot} = \frac{kT}{\hbar^2/2I} = \frac{4.115\times10^{-21}}{2.105\times10^{-22}} = 19.6$$

(The full sum over J gives 19.9, so the integral is a good approximation when $\hbar^2/2IkT \ll 1$.)

(c)

$$\ln q_{rot} = \ln T + \ln\left(\frac{2Ik}{\hbar^2}\right) \qquad \left(\frac{\partial \ln q_{rot}}{\partial T}\right)_V = \frac{1}{T}$$

$$\langle E\rangle_{rot} = NkT^2 \cdot \frac{1}{T} = NkT \qquad N = N_A: \ \bar{U}_{rot} = RT$$

$$C_{V,rot} = \left(\frac{\partial \bar{U}_{rot}}{\partial T}\right)_V = R$$

A linear molecule has 2 rotational degrees of freedom, each contributing ½RT.

Problem 5

For the partition function of Problem 2,

$$Q(N,V,\beta) = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2}(V-Nb)^N e^{\beta aN^2/V}$$

(a) Calculate <E>.

(b) Calculate C_v. How does it compare with that of an ideal monoatomic gas?

(c) Calculate $(\partial\langle E\rangle/\partial V)_{N,T}$ and explain the sign of the a-term in <E>.

Solution

(a) Separating the terms that depend on β,

$$\ln Q = -\frac{3N}{2}\ln\beta + \frac{\beta aN^2}{V} + \text{terms in N and V only}$$

$$\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = -\frac{3N}{2\beta} + \frac{aN^2}{V}$$

$$\langle E\rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = \frac{3}{2}NkT - \frac{aN^2}{V}$$

(b)

$$C_V = \left(\frac{\partial \langle E\rangle}{\partial T}\right)_{N,V} = \frac{3}{2}Nk \qquad \left(= \frac{3}{2}R \text{ per mole}\right)$$

This is the same as for an ideal monoatomic gas: the a-term does not depend on T, and b does not appear in <E> at all.

(c)

$$\left(\frac{\partial \langle E\rangle}{\partial V}\right)_{N,T} = \frac{aN^2}{V^2}$$

The attractive interactions (measured by a) lower the energy by aN^2/V. When the gas expands, the molecules move further apart, so the energy increases.

Check, using $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$ with P from Problem 2: $NkT/(V - Nb) - [NkT/(V - Nb) - aN^2/V^2] = aN^2/V^2$.

Problem 6

Using the result of Problem 1, calculate the molar heat capacity of diamond in the Einstein model at 298 K and at 1000 K. Take $h\nu/k = 1320$ K.

(a) Calculate the frequency ν.

(b) Calculate C_V at 298 K and at 1000 K.

(c) Compare your answers with the high-temperature limit, 3R, and comment.

Solution

(a)

$$\nu = \frac{k(1320\ \mathrm{K})}{h} = \frac{(1.381\times10^{-23})(1320)}{6.626\times10^{-34}} = 2.75\times10^{13}\ \mathrm{s^{-1}}$$

(b) From Problem 1, with $x = h\nu/kT$,

$$C_V = 3R\,\frac{x^2 e^{-x}}{(1-e^{-x})^2}$$

At 298 K: $x = 1320/298 = 4.43$

$$C_V = (24.94)\,\frac{(4.43)^2(0.01192)}{(1-0.01192)^2} = (24.94)(0.2396) = 5.98\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

At 1000 K: $x = 1320/1000 = 1.32$

$$C_V = (24.94)\,\frac{(1.32)^2(0.2671)}{(1-0.2671)^2} = (24.94)(0.8666) = 21.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

(c) $3R = 24.94\ \mathrm{J\ K^{-1}\ mol^{-1}}$. At 298 K, C_v is only 24% of $3R$; at 1000 K it is 87% of $3R$.

For diamond $h\nu >> kT$ at room temperature, so most atoms are in the lowest vibrational level and the vibrations contribute little to C_v. The high-temperature limit $3R$ is reached only when $kT >> h\nu$, i.e. $T >> 1320$ K.