Statistical Mechanics

Newton's laws in principle tell us how anything works

But in a system with many particles, the actual computations can become complicated.

We will therefore be happy to get some 'average' or approximate behavior of the system that will be useful for practical purposes

Describing this average dynamics is the goal of thermodynamics

A microscopic level fundamental understanding of thermodynamics was found later, and this field is called statistical mechanics

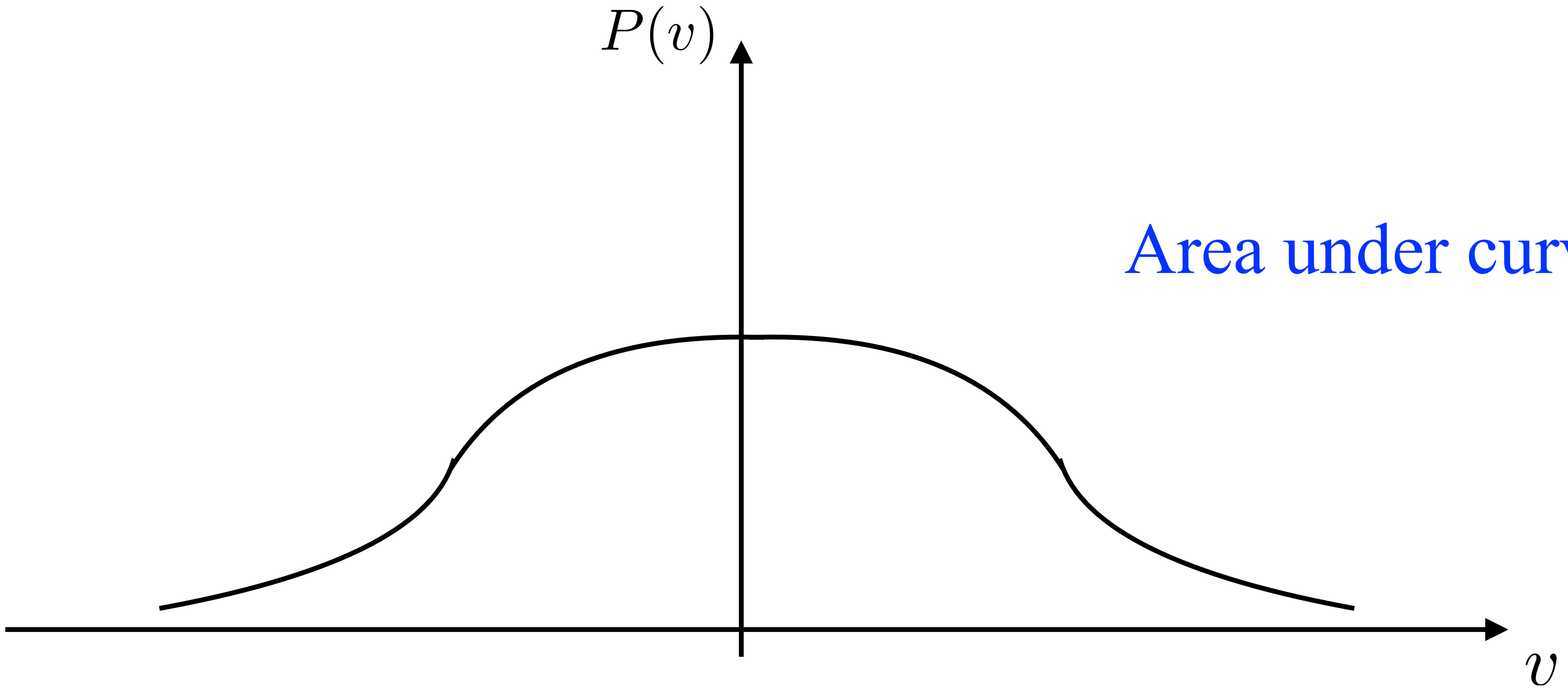
Average energy

Suppose we have probability p_i to have energy E_i

Then the average energy is

$$\boxed{\langle E \rangle = \frac{\sum_i P_i E_i}{\sum_i P_i}}$$

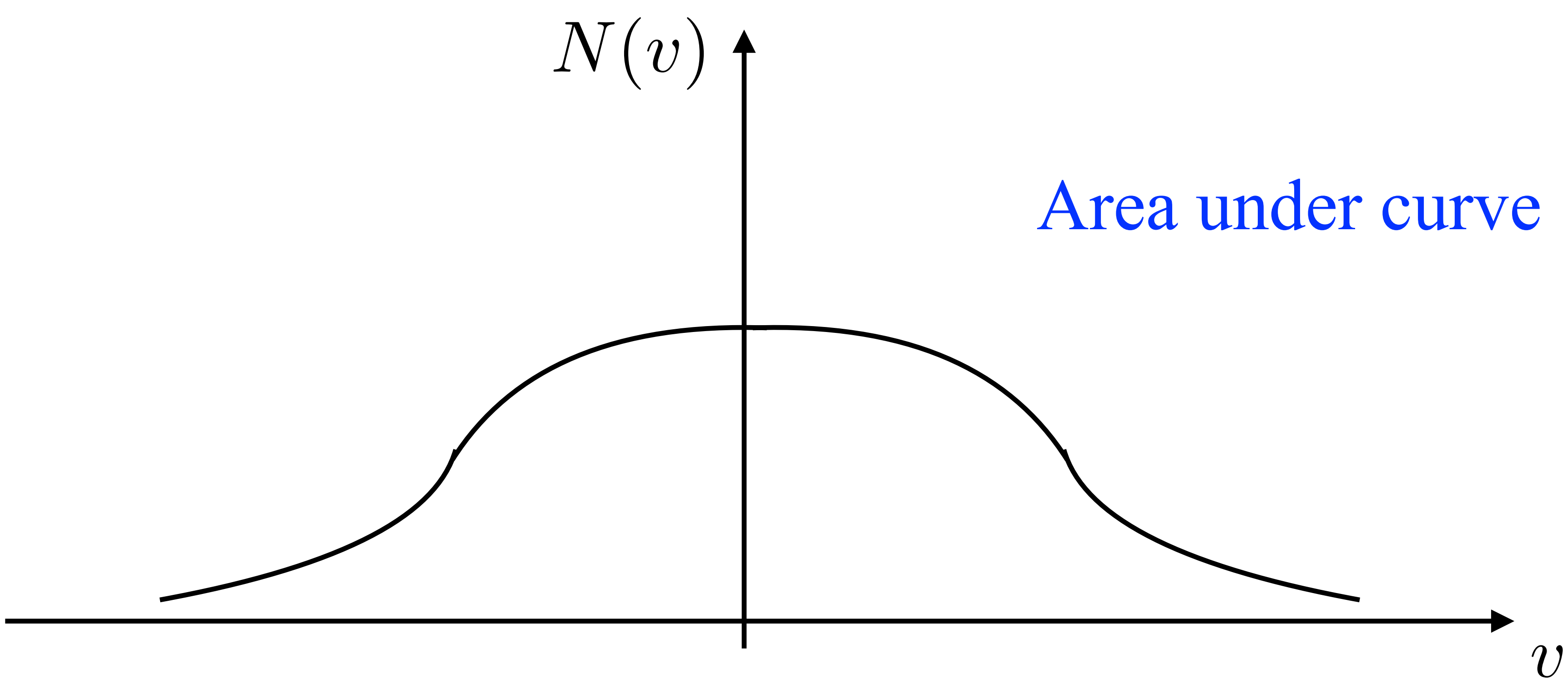
Continuous variables: Probability for any given value is zero, but we have a probability for a range



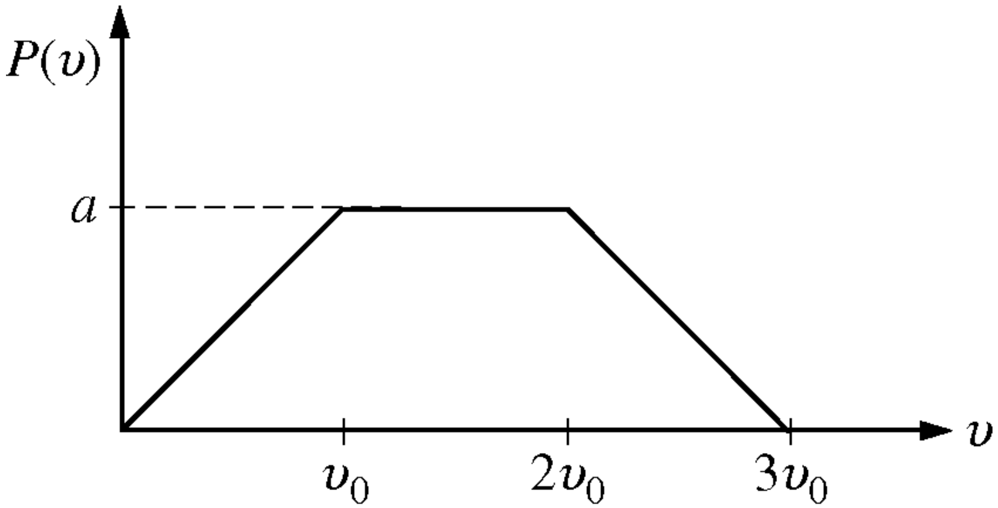
Area under curve $\int P(v)dv = 1$

Sometimes we may give the number of particles per unit velocity range

$N(v)dv$ particles have momentum between v and $v + dv$



Area under curve $\int N(v)dv = N_{total}$



56. A sample of N molecules has the distribution of speeds shown in the figure above. $P(v)dv$ is an estimate of the number of molecules with speeds between v and $v + dv$, and this number is nonzero only up to $3v_0$, where v_0 is constant. Which of the following gives the value of a ?

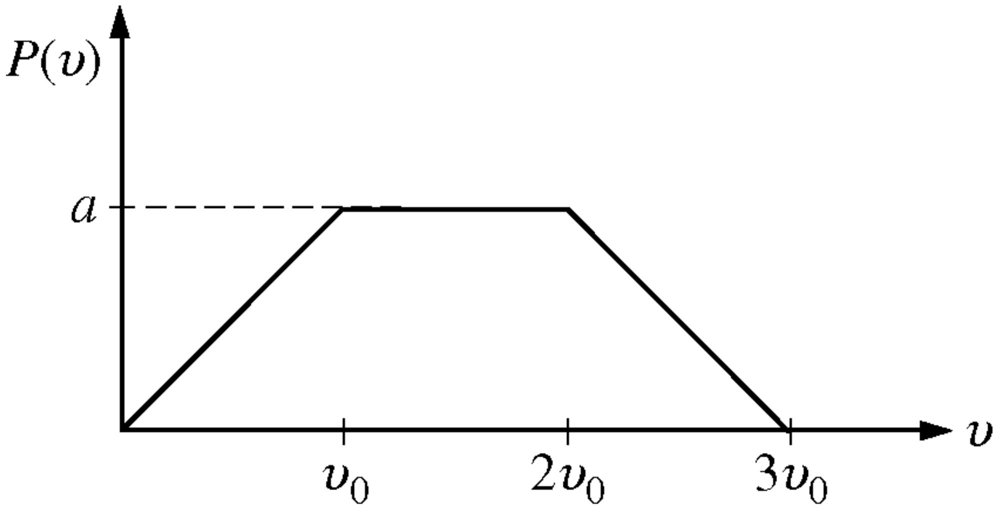
(A) $a = \dfrac{N}{3v_0}$

(B) $a = \dfrac{N}{2v_0}$

(C) $a = \dfrac{N}{v_0}$

(D) $a = \dfrac{3N}{2v_0}$

(E) $a = N$



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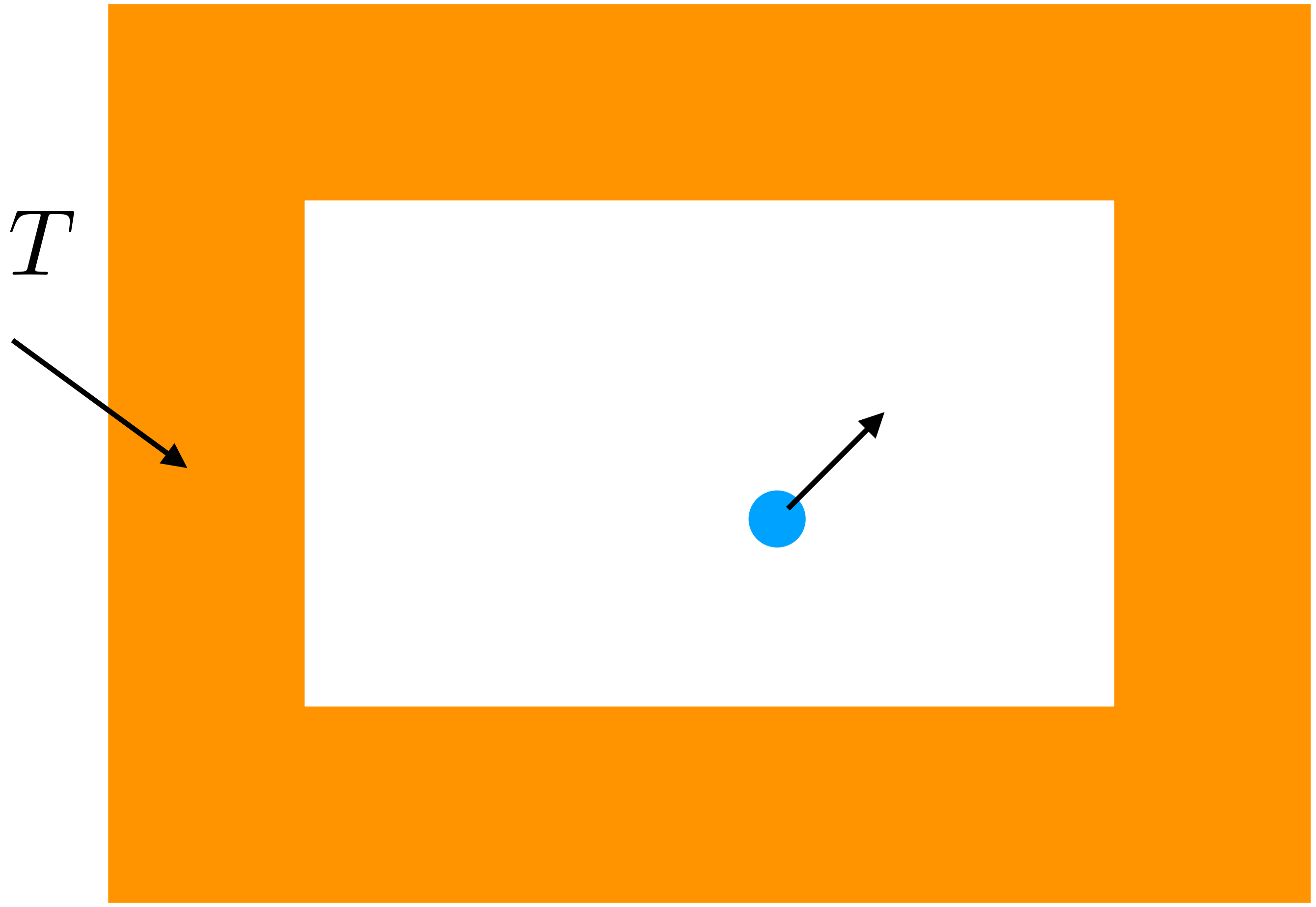
Hot bath,
temperature T



The particle can get energy
from the hot walls
when it
touches them

Basic law of Statistical Mechanics: Probability for the particle to have energy E

$$\boxed{P \propto e^{-\frac{E}{kT}}}$$

Here $k = 1.38 \times 10^{-23}\, J\, K^{-1}$ is the Boltzmann constant

77. An ensemble of systems is in thermal equilibrium with a reservoir for which $kT = 0.025$ eV. State A has an energy that is 0.1 eV above that of state B. If it is assumed the systems obey Maxwell-Boltzmann statistics and that the degeneracies of the two states are the same, then the ratio of the number of systems in state A to the number in state B is

(A) e^{+4}

(B) $e^{+0.25}$

(C) 1

(D) $e^{-0.25}$

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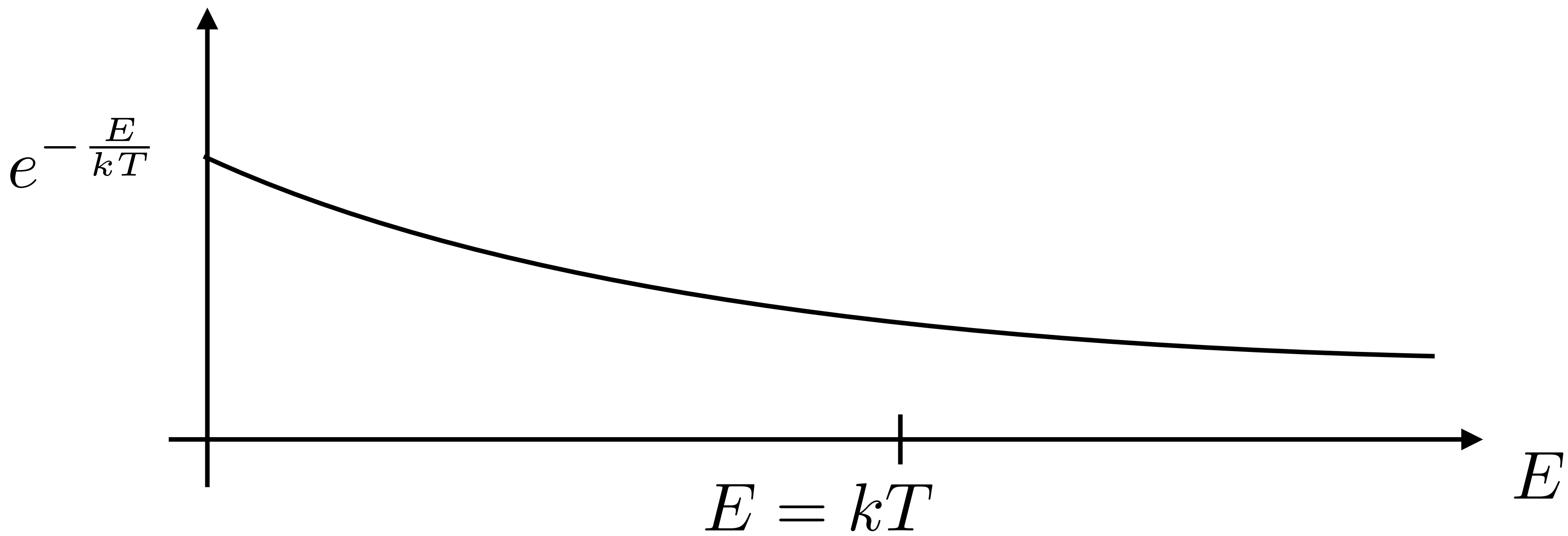
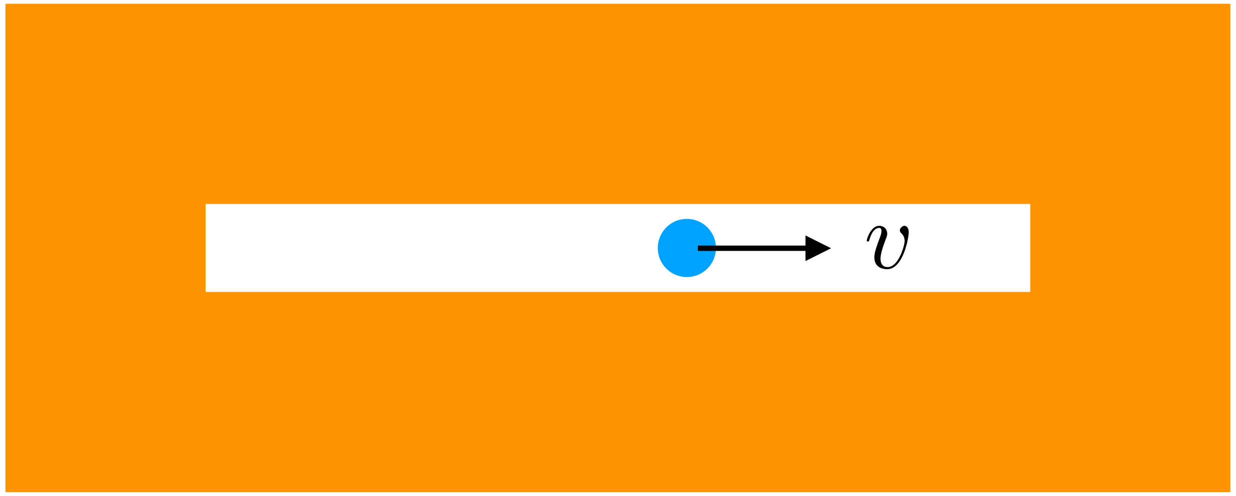


For each degree of freedom, $\boxed{\langle E \rangle = \frac{1}{2}kT}$

A state with lower energy is more likely ...

First consider the 1-dimensional problem

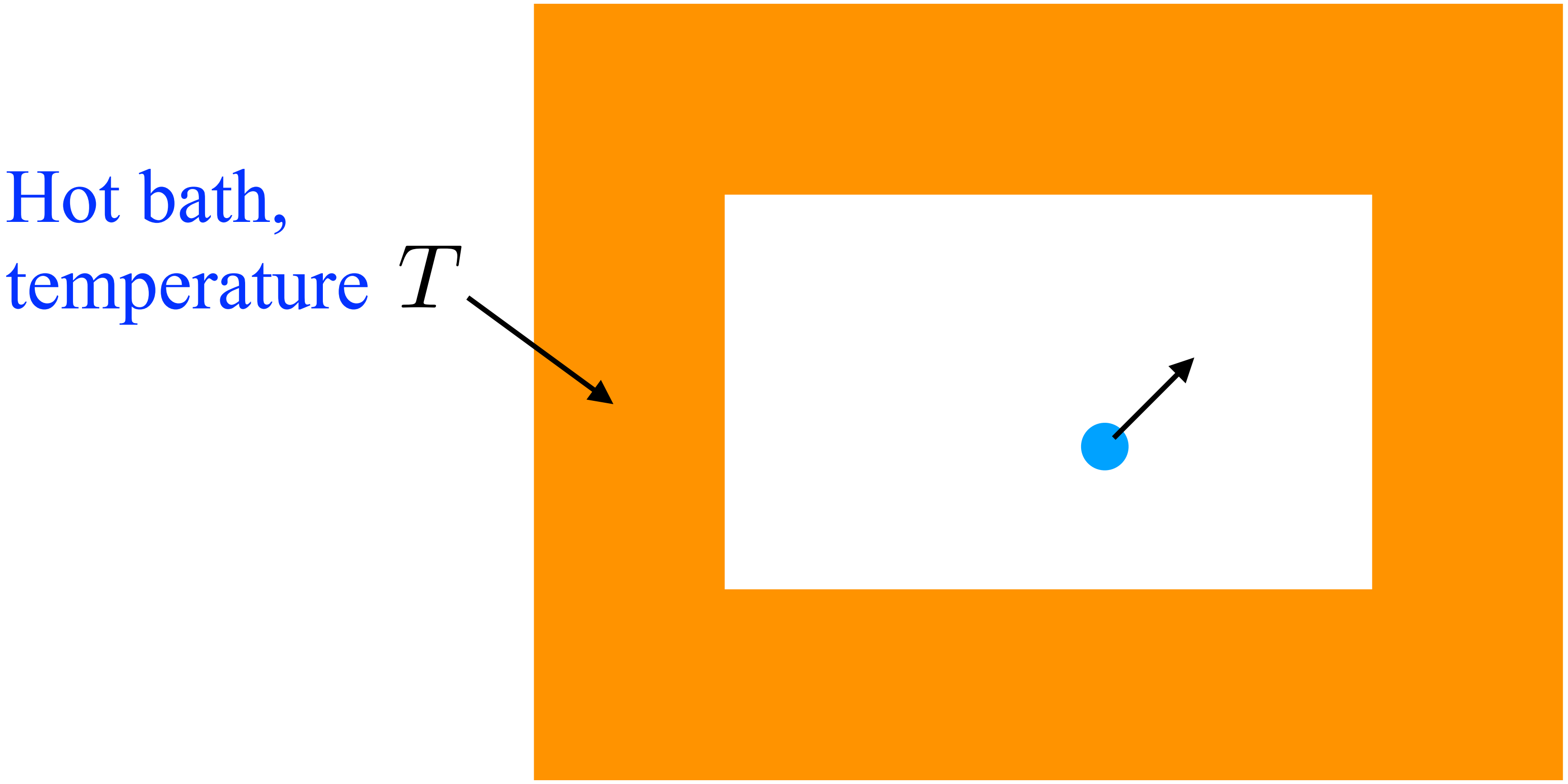


$$\boxed{P \propto e^{-\frac{E}{kT}}}$$

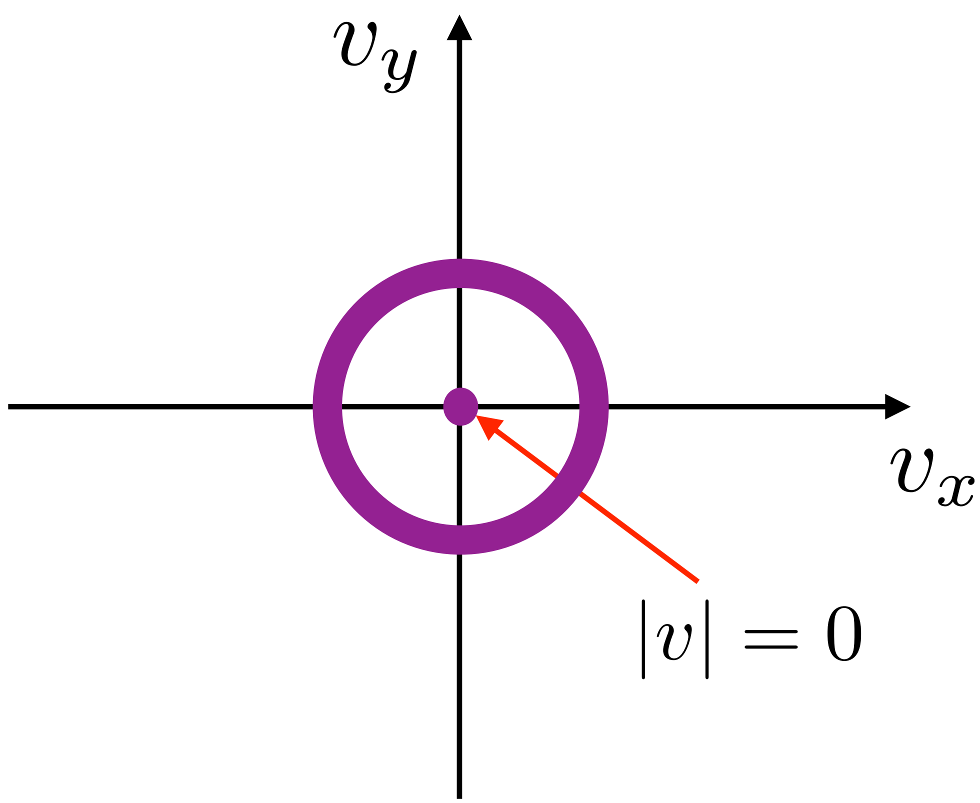
$$E = \frac{1}{2}mv^2$$

$$P(v) \propto e^{-\frac{mv^2}{2kT}}$$

The most likely speed is $v = 0$



$$P \propto e^{-\frac{(v_x^2+v_y^2)}{2kT}}$$



Many velocities $\vec{v}$ correspond to the same speed v

Higher speeds are suppressed because they have more energy

Higher speeds are enhanced because there are more possible velocities for higher speeds

57. Which of the following statements is (are) true for a Maxwell-Boltzmann description of an ideal gas of atoms in equilibrium at temperature T?

I. The average velocity of the atoms is zero.
II. The distribution of the speeds of the atoms has a maximum at $\upsilon = 0$.
III. The probability of finding an atom with zero kinetic energy is zero.

(A) I only
(B) II only
(C) I and II
(D) I and III
(E) II and III

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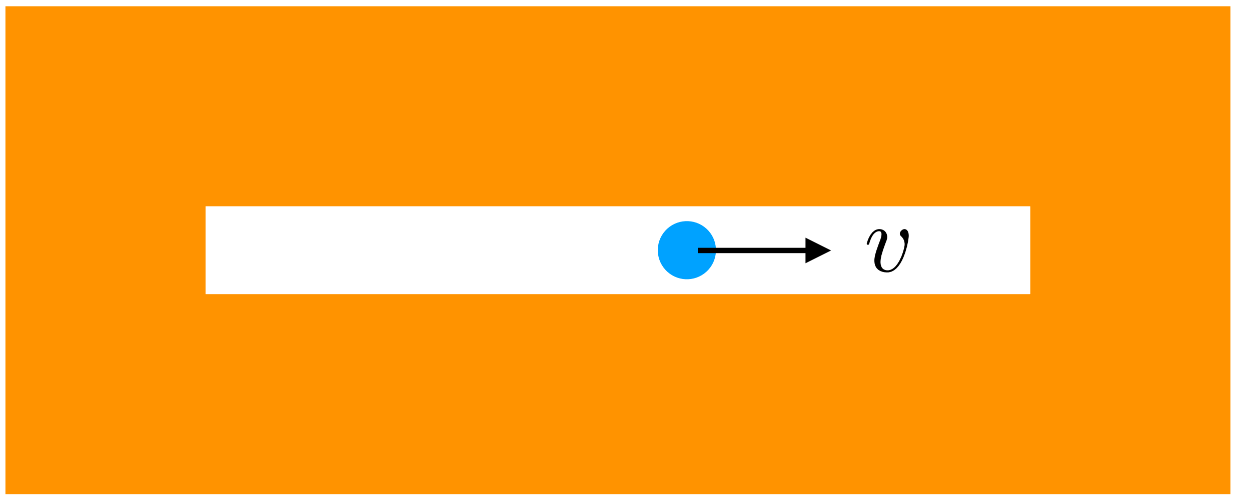
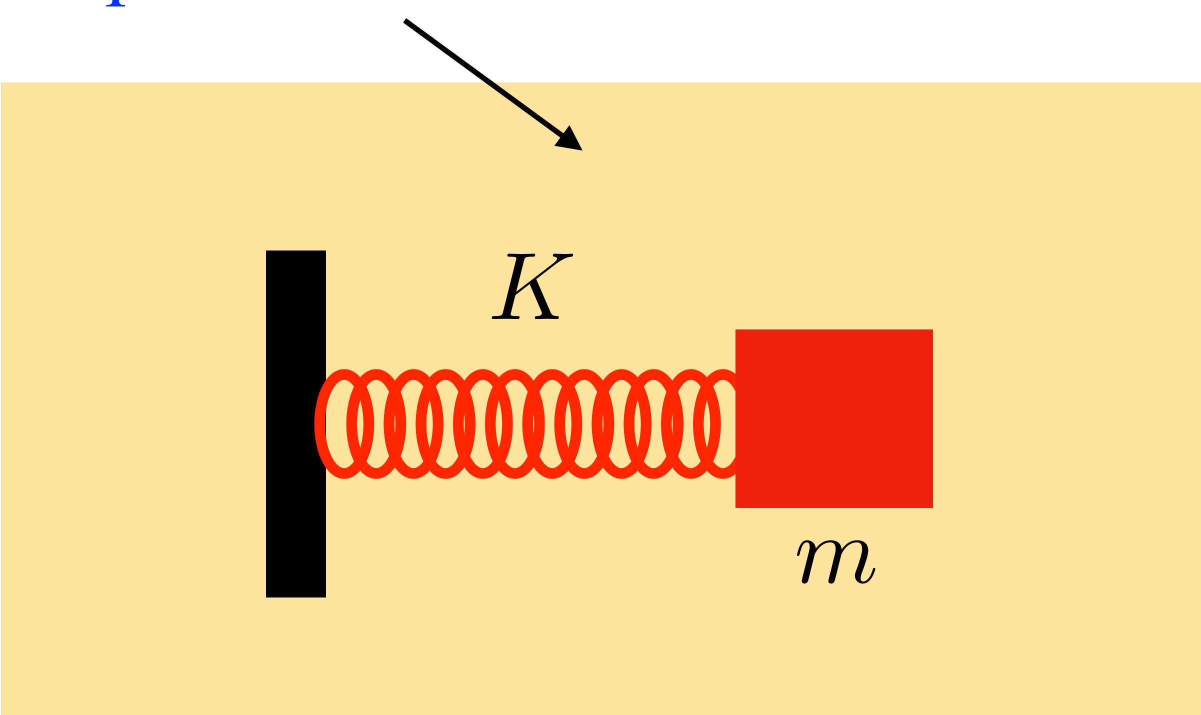
For each degree of freedom, $\boxed{\langle E \rangle = \frac{1}{2} kT}$



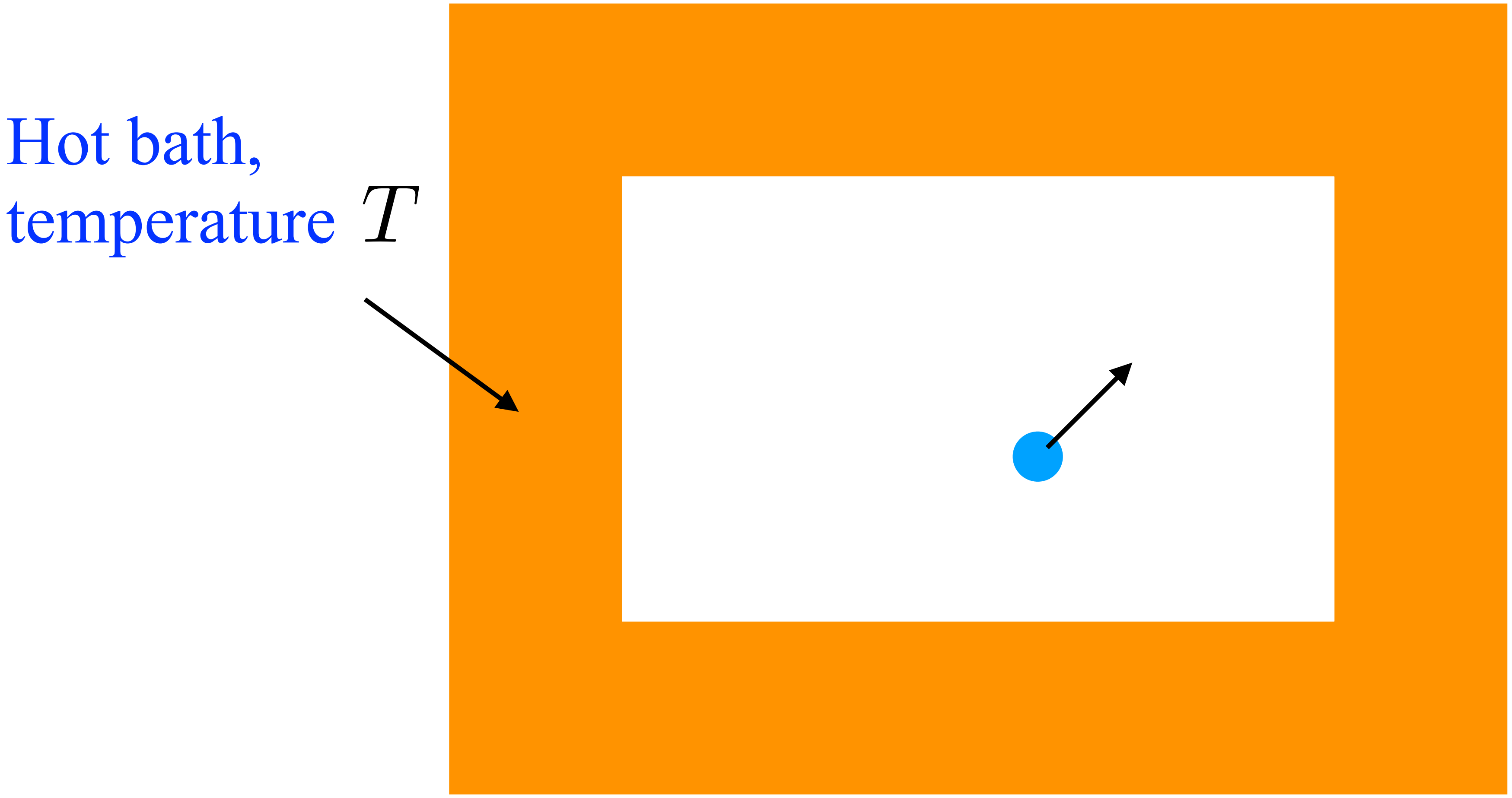
$$\langle E \rangle = \langle \frac{1}{2} m v^2 \rangle = \frac{1}{2} kT$$

Hot bath,
temperature T



$$\langle E \rangle = \langle \frac{1}{2} m v^2 \rangle + \langle \frac{1}{2} K x^2 \rangle$$

$$= \frac{1}{2} kT + \frac{1}{2} kT = kT$$



Particle in 3-d

$$\langle E \rangle \;=\; \langle \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \rangle \;=\; \frac{3}{2}\,kT$$

5. A three-dimensional harmonic oscillator is in thermal equilibrium with a temperature reservoir at temperature T. The average total energy of the oscillator is

(A) $\frac{1}{2}kT$

(B) kT

(C) $\frac{3}{2}kT$

(D) $3kT$

(E) $6kT$

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48. A gaseous mixture of O_2 (molecular mass 32 u) and N_2 (molecular mass 28 u) is maintained at constant temperature. What is the ratio $\dfrac{v_{rms}(N_2)}{v_{rms}(O_2)}$ of the root-mean-square speeds of the molecules?

(A) $\dfrac{7}{8}$

(B) $\sqrt{\dfrac{7}{8}}$

(C) $\sqrt{\dfrac{8}{7}}$

(D) $\left(\dfrac{8}{7}\right)^2$

(E) $\ln\left(\dfrac{8}{7}\right)$

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Avagadro number $N = 6 \times 10^{23}$ (1 mole)

Avagadro number of H atoms weigh 1 gram

Avagadro number of He atoms weigh 4 grams

Molar mass of H = 1gm = mass of H atom times N

Molar mass of He = 4 gm = mass of He atom times N

We define $\boxed{k\,N = R}$ $R = 8.31\ JK^{-1}/mole$

One degree of freedom $\langle E \rangle = \frac{1}{2} kT$

N degrees of freedom $\langle E \rangle = \frac{1}{2} NkT = \frac{1}{2} RT$

9. The root-mean-square speed of molecules in an ideal gas of molar mass M at temperature T is

(A) 0

(B) $\sqrt{\dfrac{RT}{M}}$

(C) $\dfrac{RT}{M}$

(D) $\sqrt{\dfrac{3RT}{M}}$

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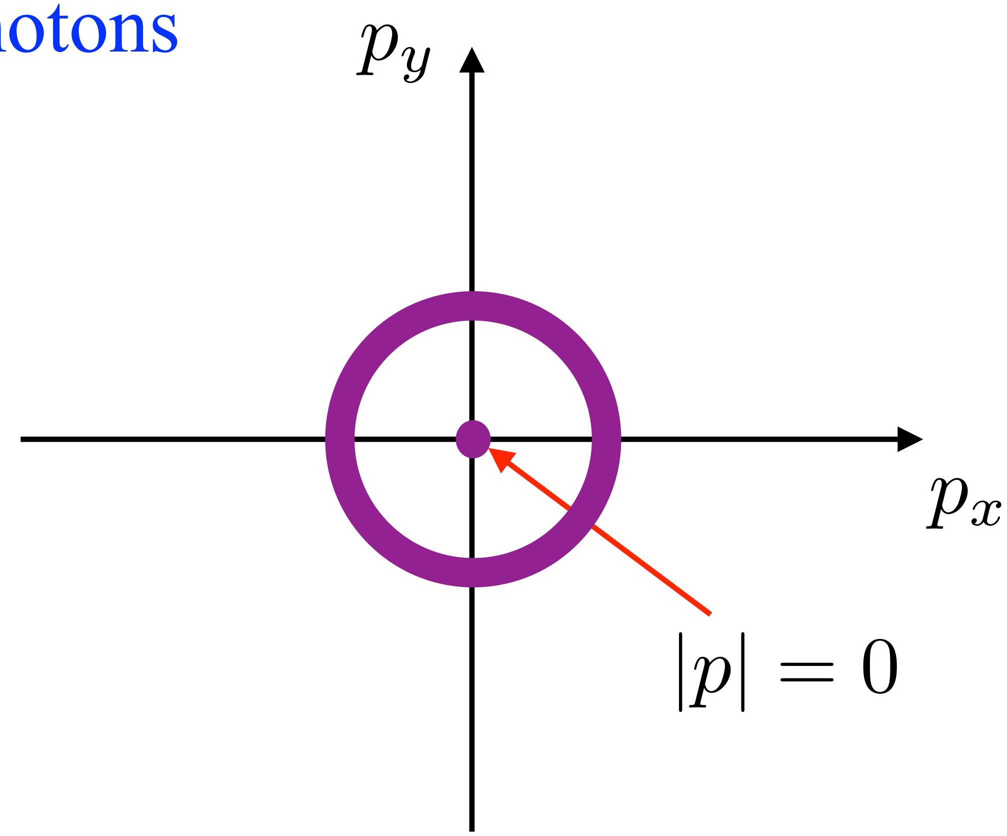
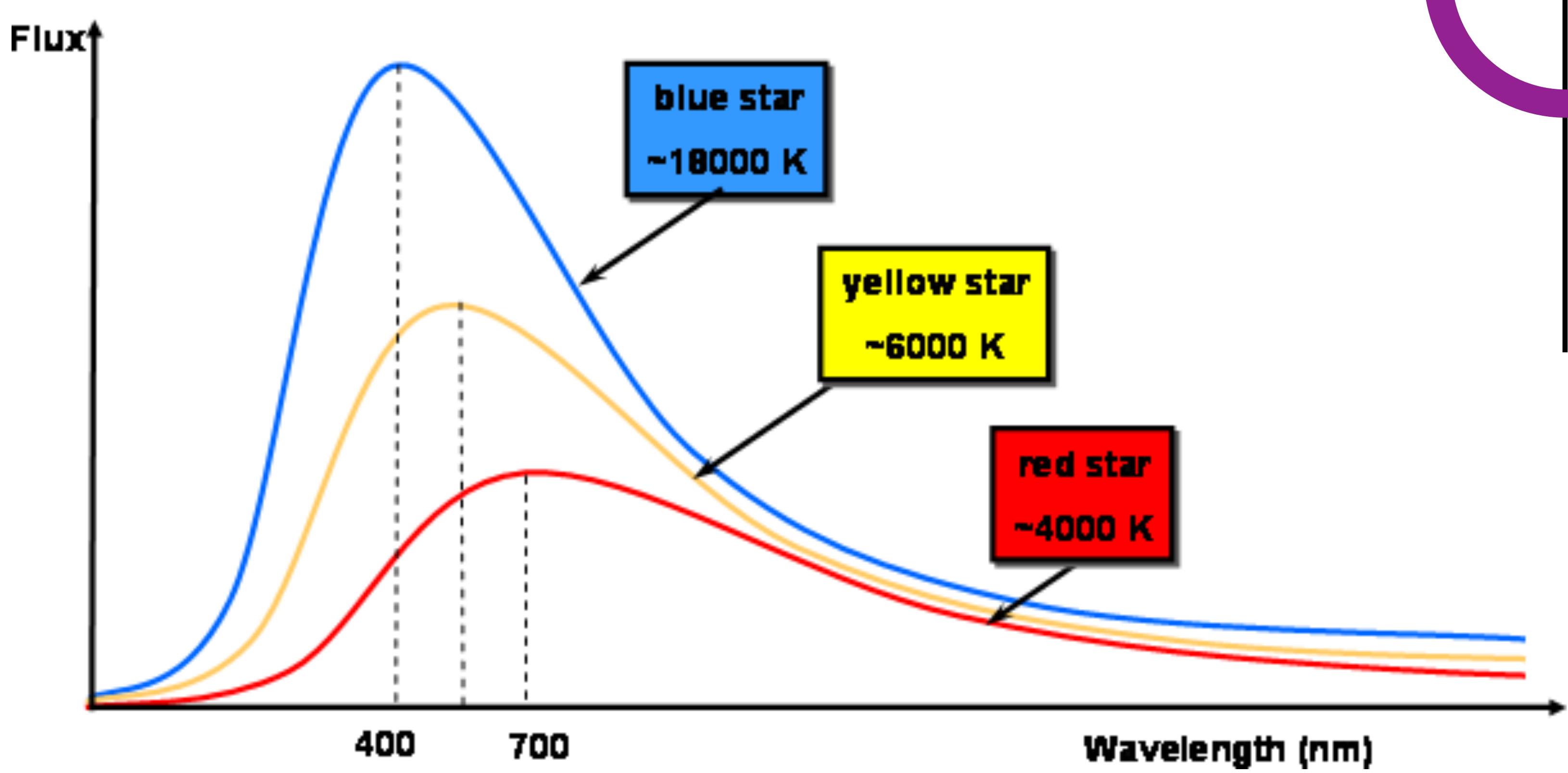
Blackbody radiation is made of photons

$$\boxed{P \sim e^{-\frac{E}{kT}}}$$



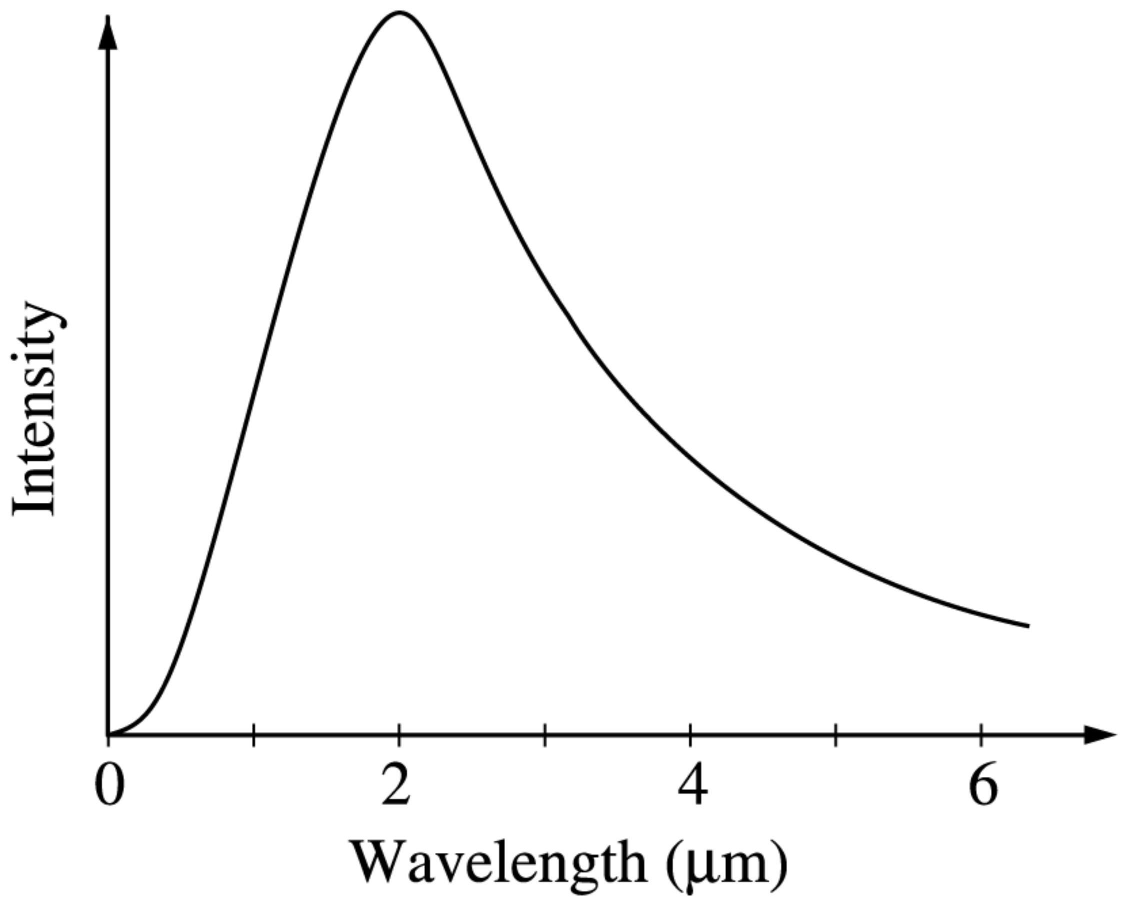


Wien displacement constant $W = 2.9 \times 10^{-3}\, m\, K$

$$\boxed{\frac{W}{\lambda_{peak}} = T_{peak}}$$

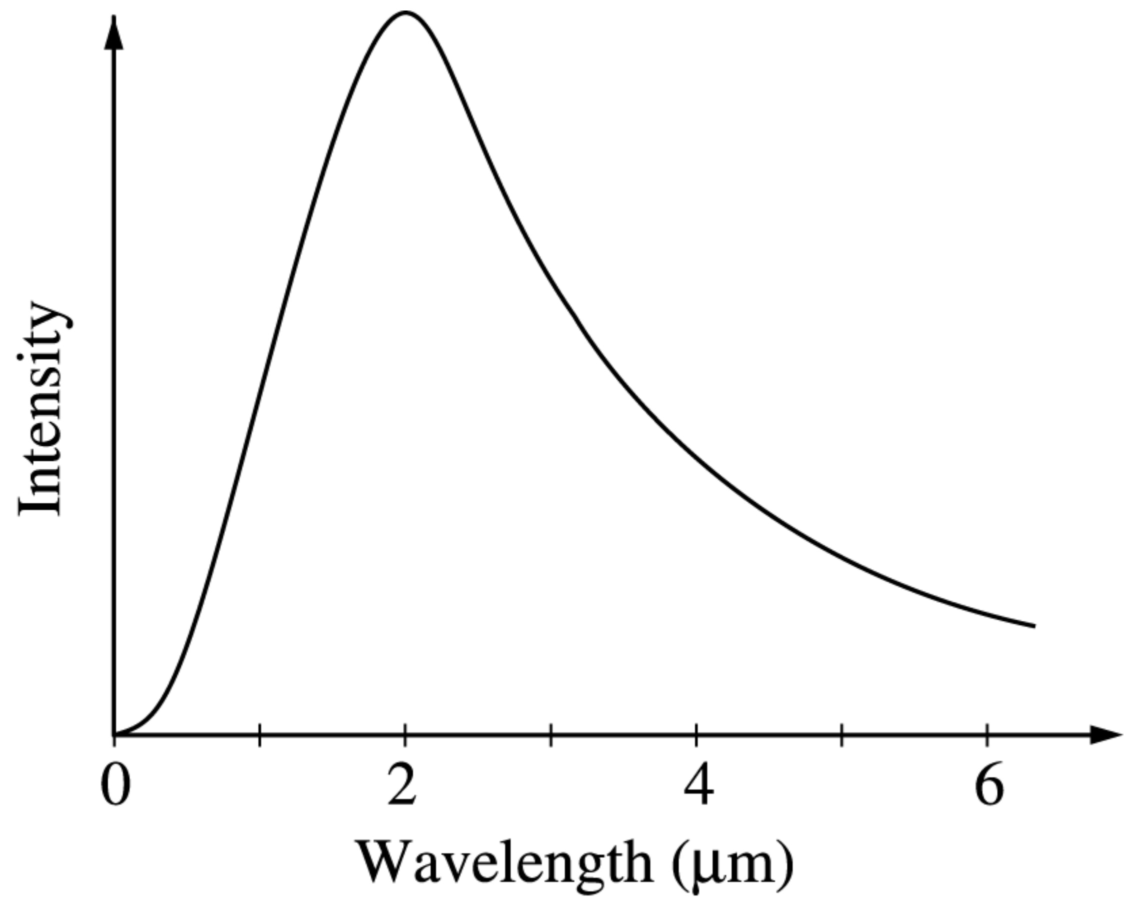
Wien displacement law:

Double T ➔ double peak E ➔ halve wavelength



63. The distribution of relative intensity $I(\lambda)$ of blackbody radiation from a solid object *versus* the wavelength λ is shown in the figure above. If the Wien displacement law constant is 2.9×10^{-3} m·K, what is the approximate temperature of the object?

(A) 10 K
(B) 50 K
(C) 250 K
(D) 1,500 K
(E) 6,250 K



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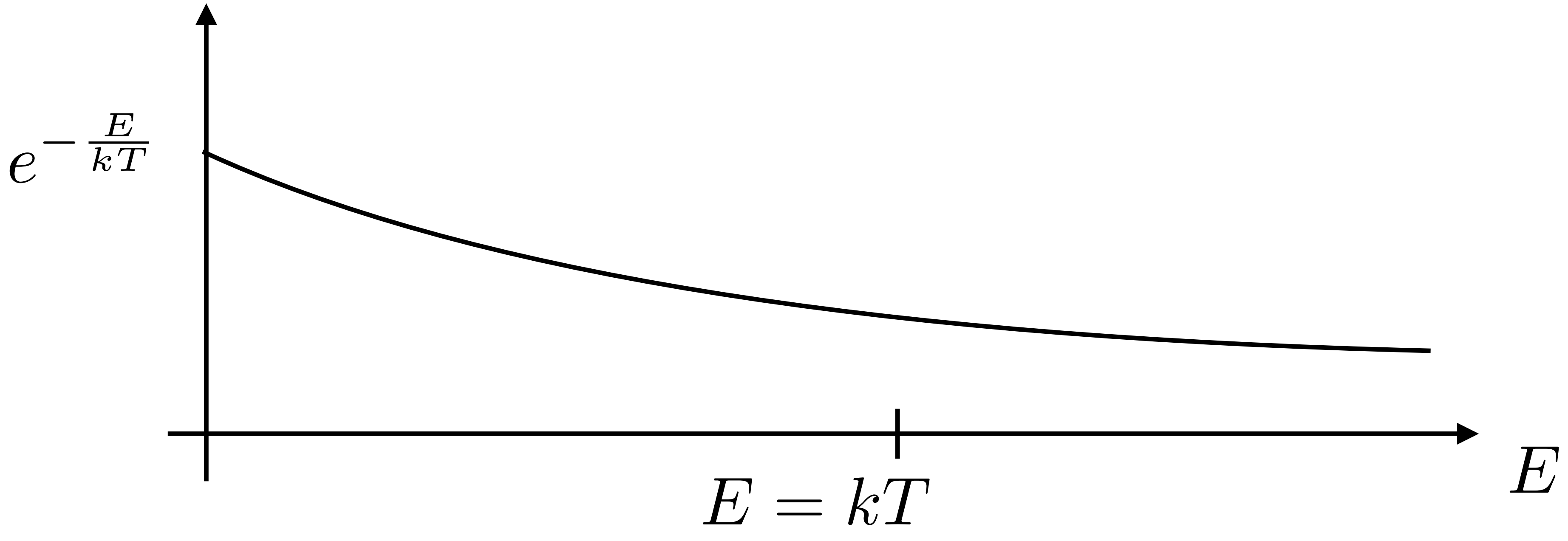
Approximations



For $x \ll 1$

$$e^{-x} \approx 1 - x + \ldots$$

Low energy

$$\boxed{e^{-\frac{E}{kT}} \approx 1 - \frac{E}{kT}}$$

$$C = 3kN_A\left(\frac{hv}{kT}\right)^2 \frac{e^{hv/kT}}{(e^{hv/kT} - 1)^2}$$

65. Einstein's formula for the molar heat capacity C of solids is given above. At high temperatures, C approaches which of the following?

(A) 0

(B) $3kN_A\left(\frac{hv}{kT}\right)$

(C) $3kN_A hv$

(D) $3kN_A$

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The partition function

The average energy is

$$\langle E \rangle = \frac{\sum_i P_i E_i}{\sum_i P_i} \quad \text{with} \quad P_i \propto e^{-\frac{E_i}{kT}}$$

To compute this, we define the Partition Function

$$\boxed{Z = \sum_i e^{-\frac{E_i}{kT}}}$$

We write $\dfrac{1}{kT} = \beta$

This gives $Z = \sum_i e^{-\beta E_i}$ $\qquad -\dfrac{\partial Z}{\partial \beta} = \sum_i e^{-\beta E_i} E_i$

$$-\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{\sum_i e^{-\beta E_i} E_i}{\sum_i e^{-\beta E_i}} = \langle E \rangle$$

98. Suppose that a system in quantum state i has energy E_i. In thermal equilibrium, the expression

$$\frac{\sum_i E_i e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$

represents which of the following?

(A) The average energy of the system
(B) The partition function
(C) Unity
(D) The probability to find the system with energy E_i
(E) The entropy of the system

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49. In a Maxwell-Boltzmann system with two states of energies ϵ and 2ϵ, respectively, and a degeneracy of 2 for each state, the partition function is

(A) $e^{-\epsilon/kT}$

(B) $2e^{-2\epsilon/kT}$

(C) $2e^{-3\epsilon/kT}$

(D) $e^{-\epsilon/kT} + e^{-2\epsilon/kT}$

(E) $2[e^{-\epsilon/kT} + e^{-2\epsilon/kT}]$

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An unusual situation

76. The mean kinetic energy of the conduction electrons in metals is ordinarily much higher than kT because

    (A) electrons have many more degrees of freedom than atoms do
    (B) the electrons and the lattice are not in thermal equilibrium
    (C) the electrons form a degenerate Fermi gas
    (D) electrons in metals are highly relativistic
    (E) electrons interact strongly with phonons

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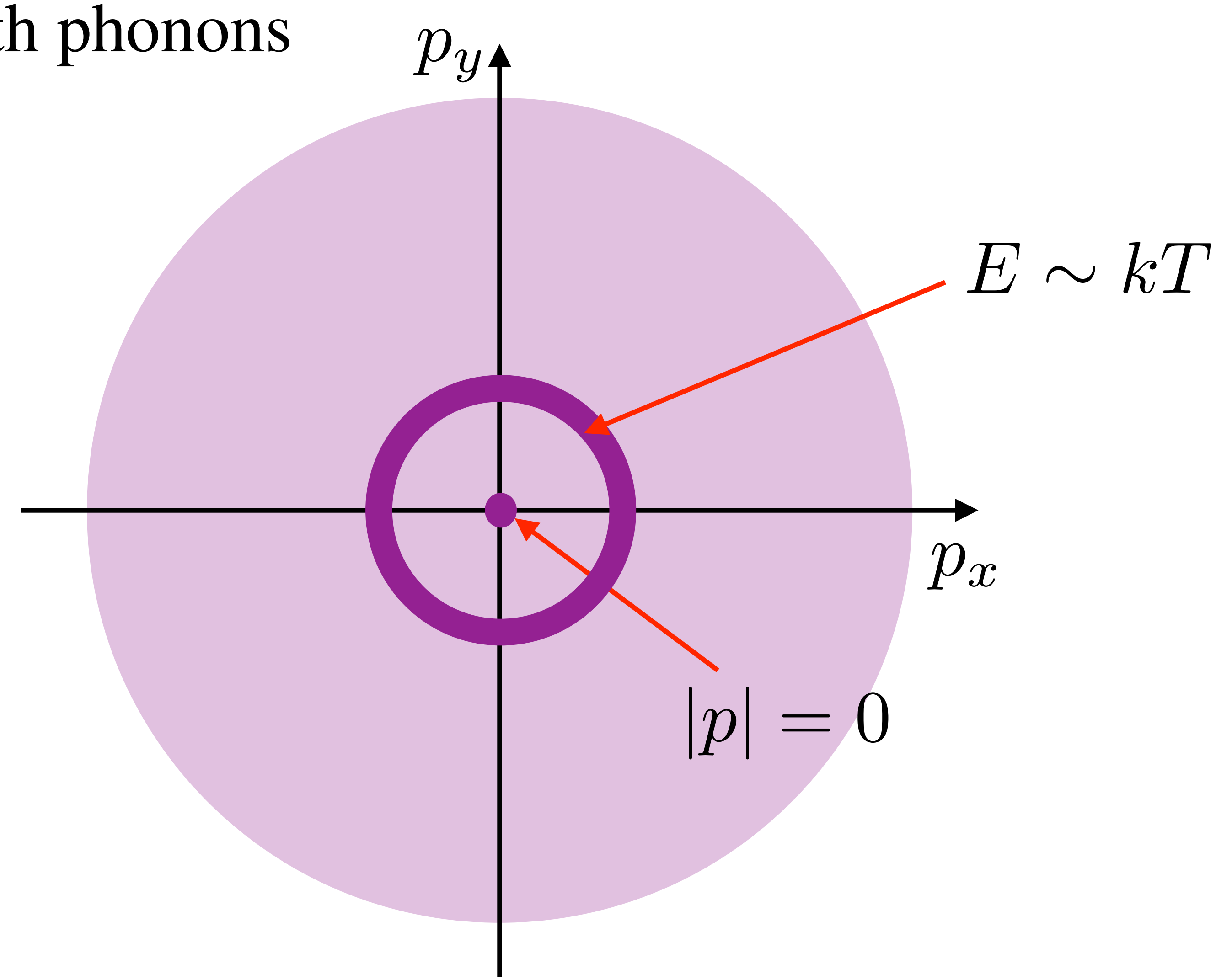
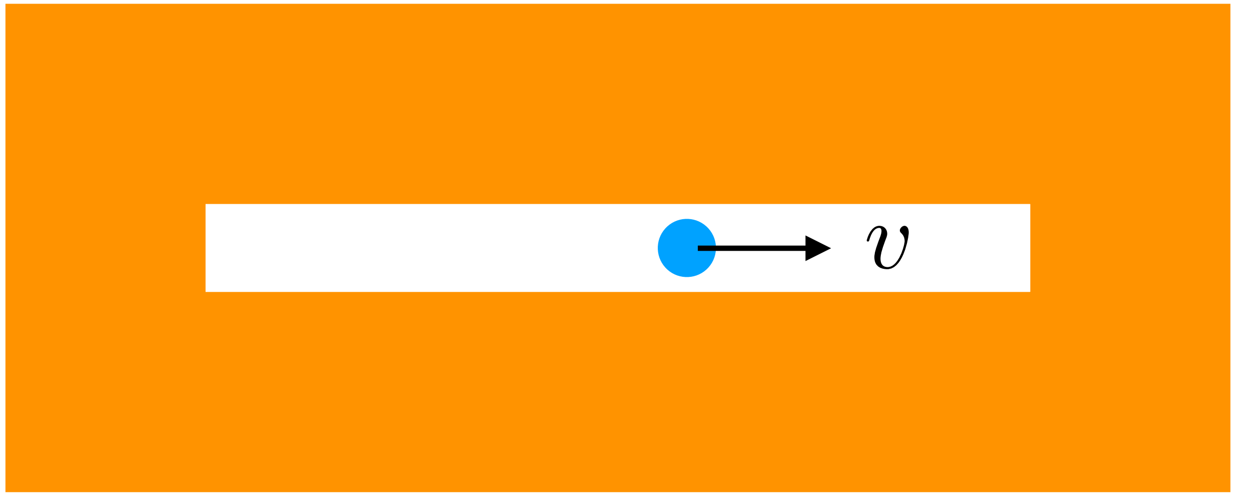


Deriving $\langle E \rangle = \frac{1}{2}kT$

First consider the 1-dimensional problem



$$\boxed{P \ \sim \ e^{-\frac{E}{kT}}}$$

$$E = \frac{1}{2}mv^2$$

$$P(v) \propto e^{-\frac{mv^2}{2kT}}$$

Adding over all possibilities : $\int_{-\infty}^{\infty} dv$

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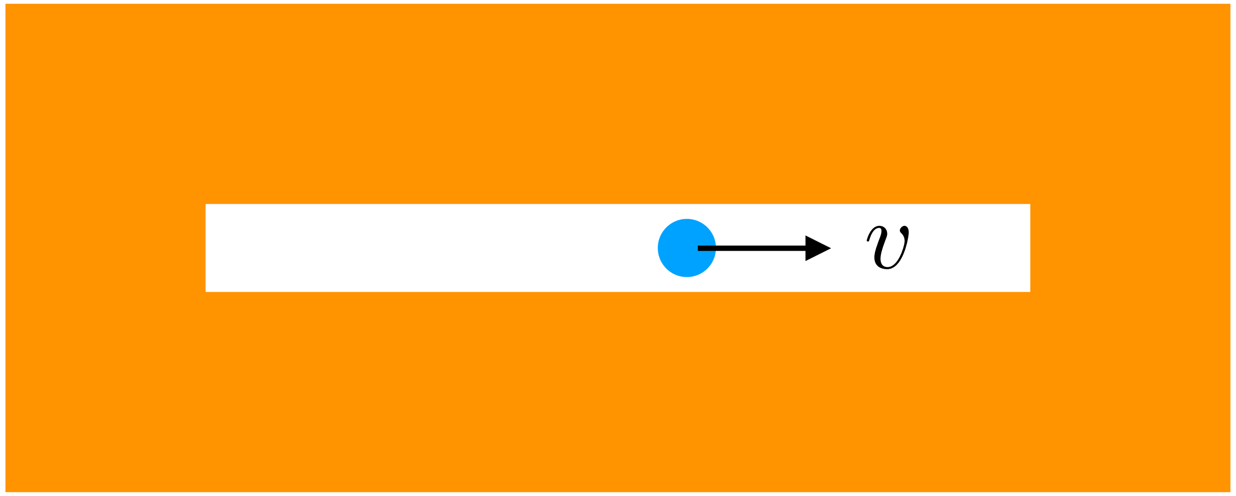


$$\langle E \rangle = \frac{\sum_i p_i E_i}{\sum_i p_i}$$

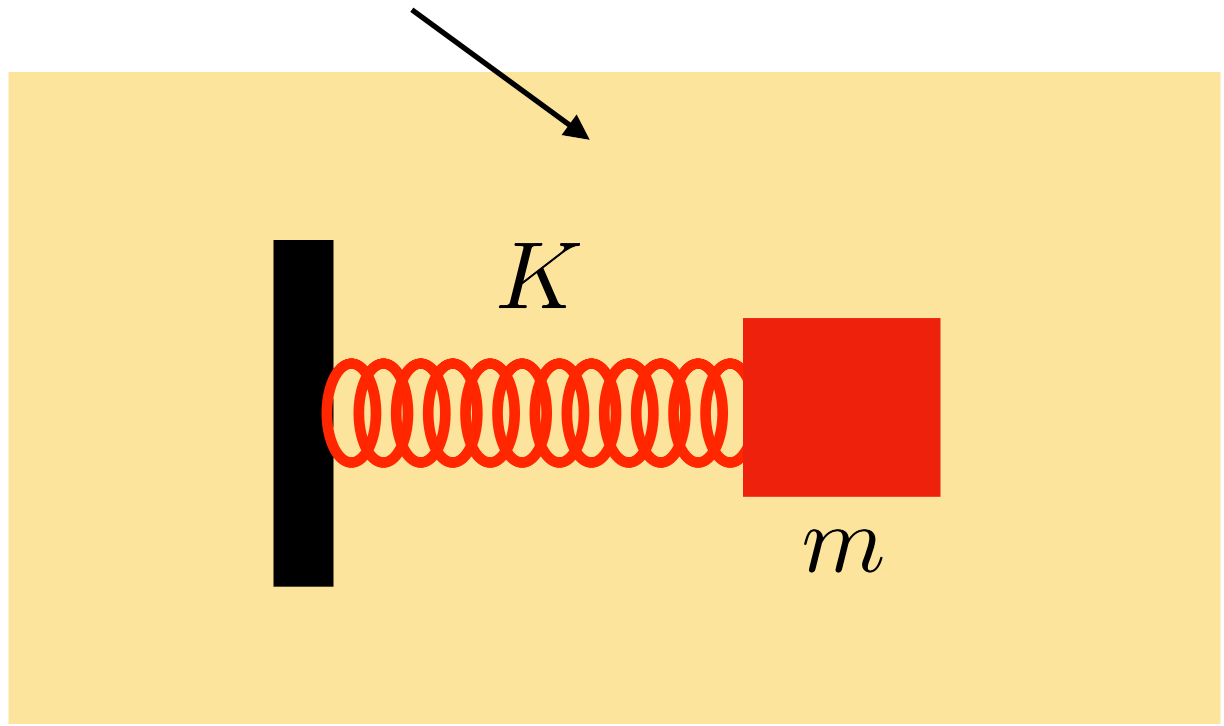
$$p \propto e^{-\frac{E}{kT}}$$

$$E = \frac{1}{2} m v^2$$

$$p(v) \propto e^{-\frac{mv^2}{2kT}}$$

$$\langle E \rangle = \frac{\int_{-\infty}^{\infty} dv (\frac{1}{2} m v^2) \; e^{-\frac{mv^2}{2kT}}}{\int_{-\infty}^{\infty} dv \; e^{-\frac{mv^2}{2kT}}} = \frac{1}{2} kT$$

Hot bath,
temperature T



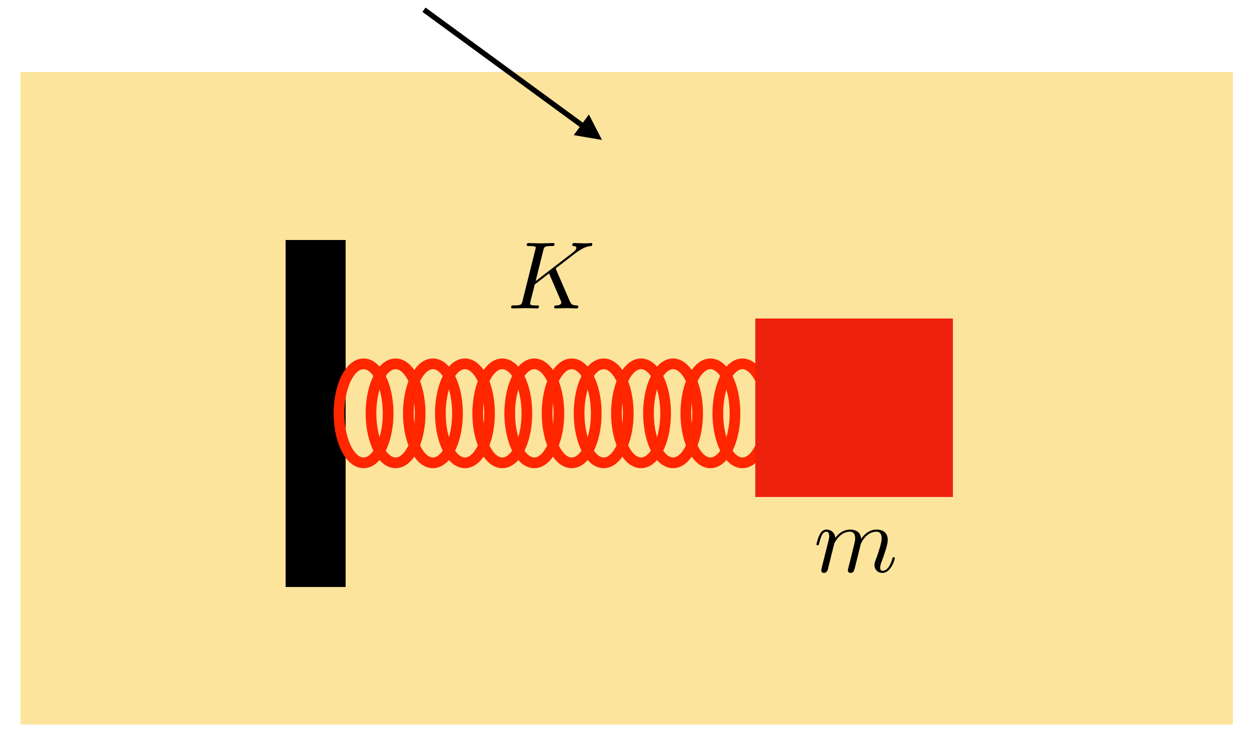
$$\boxed{p \propto e^{-\frac{E}{kT}}}$$

$$E = \frac{1}{2}mv^2 + \frac{1}{2}Kx^2$$

$$p \propto e^{-\frac{mv^2}{2kT}}\, e^{-\frac{Kx^2}{2kT}}$$

Adding over all possibilities of velocity : $\int_{-\infty}^{\infty} dv$

Adding over all possibilities of position : $\int_{-\infty}^{\infty} dx$



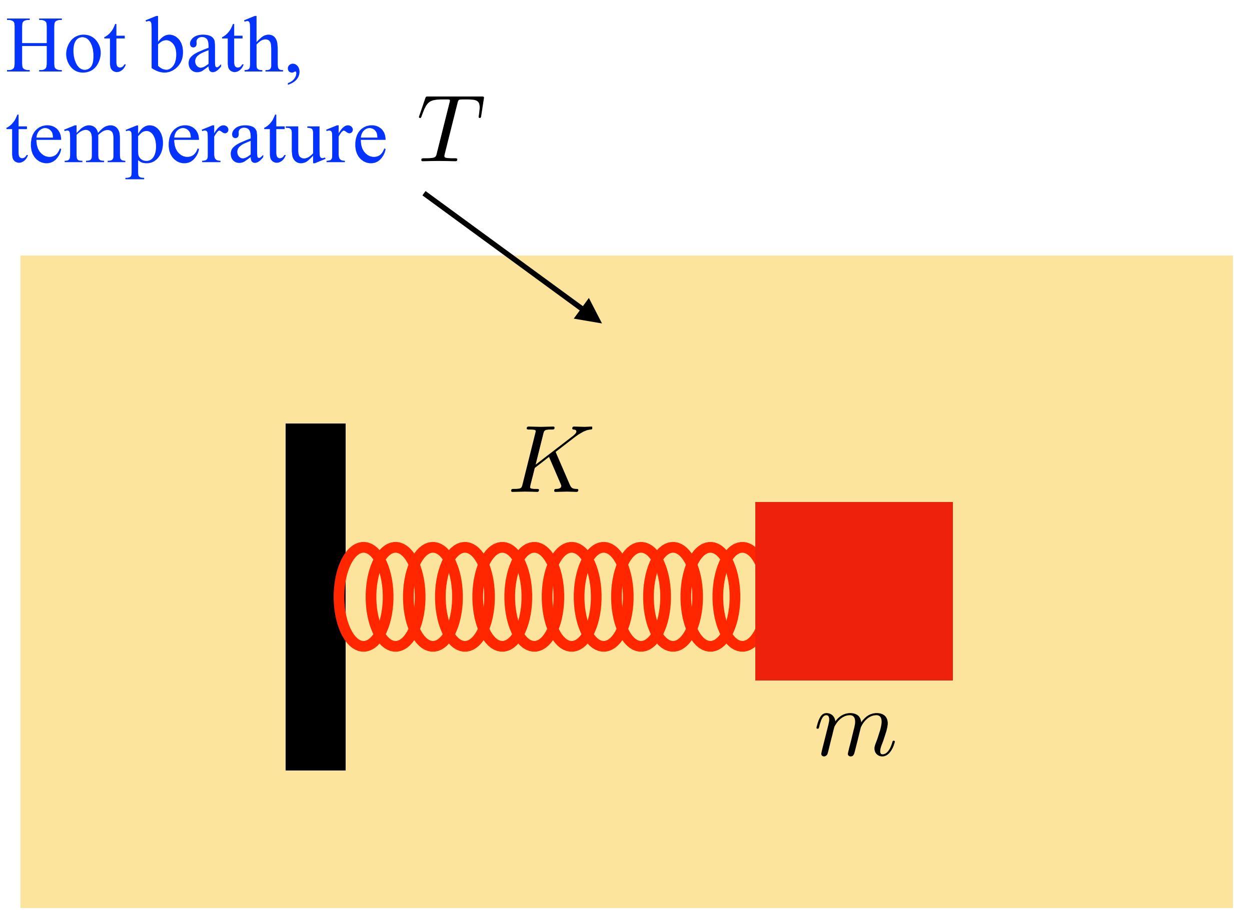
$$\boxed{p \;\propto\; e^{-\frac{E}{kT}}}$$

$$E \;=\; \frac{1}{2}mv^2 \;+\; \frac{1}{2}Kx^2$$

$$p \propto e^{-\frac{mv^2}{2kT}}\, e^{-\frac{Kx^2}{2kT}}$$

Adding over all probabilities

$$\int\int dv dx \; e^{-\frac{mv^2}{2kT}} e^{-\frac{Kx^2}{2kT}} \;=\; \left(\int dv\, e^{-\frac{mv^2}{2kT}}\right)\;\left(\int dx\, e^{-\frac{Kx^2}{2kT}}\right)$$



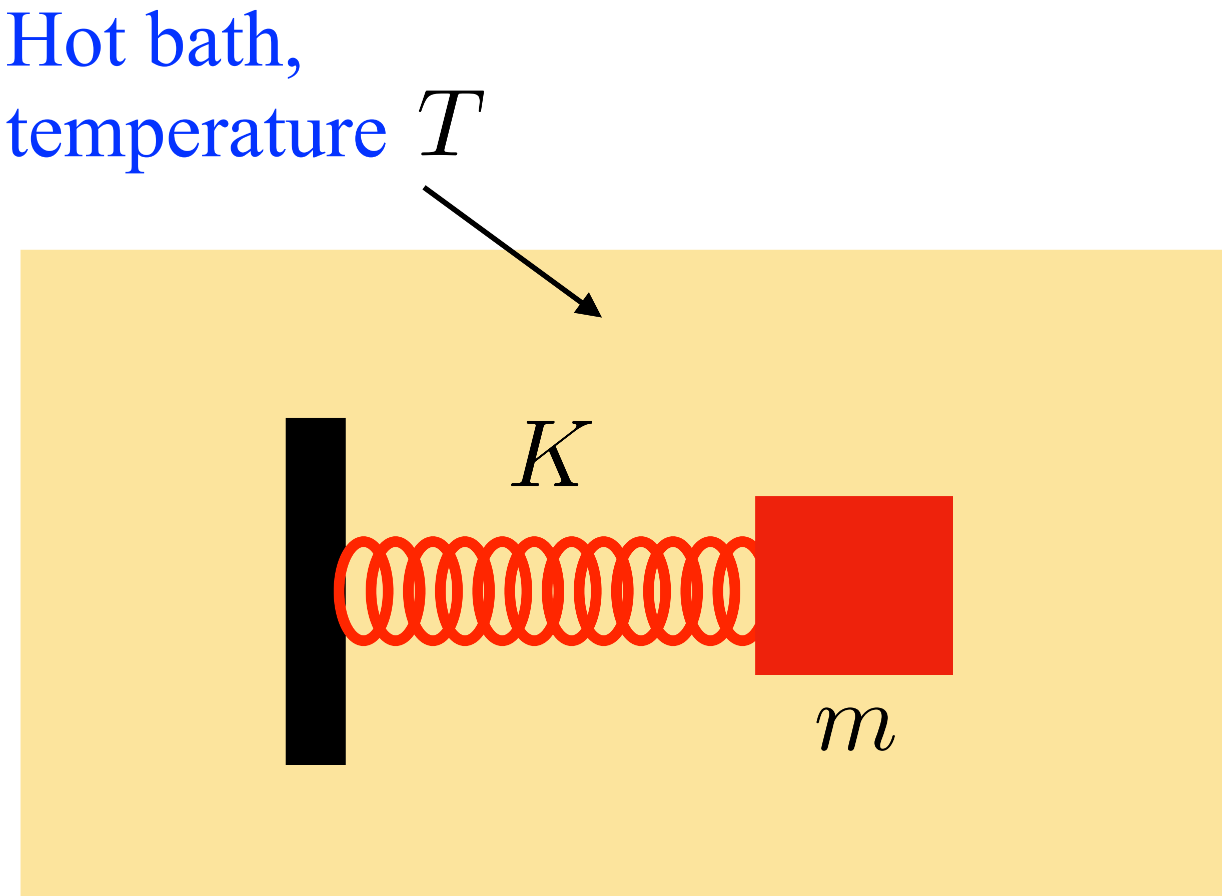
$$p \propto e^{-\frac{mv^2}{2kT}} \, e^{-\frac{Kx^2}{2kT}}$$

$$E = \frac{1}{2}mv^2 + \frac{1}{2}Kx^2$$

$$\langle \frac{1}{2}mv^2 \rangle = \frac{\int dv\, dx\, (\frac{1}{2}mv^2)\, e^{-\frac{mv^2}{2kT}} \, e^{-\frac{Kx^2}{2kT}}}{\int dv\, dx\, e^{-\frac{mv^2}{2kT}} \, e^{-\frac{Kx^2}{2kT}}}$$

$$= \frac{\int dv\, (\frac{1}{2}mv^2)\, e^{-\frac{mv^2}{2kT}}}{\int dv\, e^{-\frac{mv^2}{2kT}}} \; \frac{\int dx\, e^{-\frac{Kx^2}{2kT}}}{\int dx\, e^{-\frac{Kx^2}{2kT}}}$$

$$= \frac{1}{2} k T$$



$$p \propto e^{-\frac{mv^2}{2kT}}\; e^{-\frac{Kx^2}{2kT}}$$

$$E = \frac{1}{2}mv^2 + \frac{1}{2}Kx^2$$

$$\langle \frac{1}{2}mv^2 \rangle + \langle \frac{1}{2}Kx^2 \rangle = \frac{1}{2}kT + \frac{1}{2}kT = kT$$