BOSE-EINSTEIN CONDENSATION (16.3)

In this lecture we shall be concerned with a gas of noninteracting particles (atoms or molecules) of comparatively large mass such that quantum effects only become important at very low temperatures. The particles are assumed to comprise an ideal Bose-Einstein gas. The discussion is relevant to ^4He, which undergoes a remarkable phase transition known as *Bose-Einstein condensation.* This phenomenon is intimately related to the superfluidity of liquid helium at low temperatures.

Bosons: Are particles of integral spin that obey Bose-Einstein statistics. There is no limit to the number of bosons that can occupy any single particle state.
Ideal boson gas: Consisting of N non-interacting and indistinguishable bosons in a container of volume V held at absolute temperature T.
Bose-Einstein distribution: For an ideal BE gas (non-interactions between the indistinguishable particles) of N particles in a volume V, the most probable number of particles with energy is:

$$f(\varepsilon_i) = \frac{N^*(\varepsilon_i)}{g(\varepsilon_i)} = \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1}$$

and the continuum is:

$$f(\varepsilon) = \frac{N(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{\beta(\varepsilon-\mu)}-1}$$

$$N = \int_0^\infty N(\varepsilon)d\varepsilon = \int_0^\infty f(\varepsilon)g(\varepsilon)d\varepsilon, \qquad g(\varepsilon) = \frac{4\pi V\sqrt{2}}{h^3} m^{3/2}\varepsilon^{1/2}$$

For ^4He
at STP (standard temperature and pressure) $N = N_A = 6.02\times10^{23}$ molecules/mol,
$m = 4\times1.66\times10^{-27} = 6.65\times10^{-27}$ kg and $V = 22.4\times10^{-3}$ m^3/mole, one gets:

$$\frac{\mu}{kT} = -\ln\left(\frac{z}{N}\right) = -\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{V}{N}\right] = -\ln\left[\left(\frac{2\pi\left(6.65\times10^{-27}\text{ kg}\right)\left(1.38\times10^{-23}\text{ kg}\right)\left(273\text{ K}\right)}{\left(6.63\times10^{-34}\right)^2}\right)^{3/2}\frac{22.4}{\left(6.02\times10^{26}\right)}\right]$$

$$= -12.43$$

Note:
1- B.E. condensation can occur only when the particle number is conserved. For example, photon do not condense, they have a simpler alternative, namely, to disappear into the vacuum.
2- At $T < T_c$ the system may be looked upon as a mixture of two "phases"
i.e. the de Broglie wave length is of the order of the average particle distance. The wave function overlap and so the quantum effects are important.
Critical point: The temperature and pressure at which two phases of a substance in equilibrium with each other become identical, forming one phase.

Ideal Bose-Einstein Gas

Start with the maximum probable distribution $f(\varepsilon_i)$, where:

$$f(\varepsilon_i) = \frac{N_i^*}{g_i} = \frac{1}{e^{\alpha+\beta\,\varepsilon_i}-1}\,, \qquad \alpha = -\mu\beta \tag{1}$$

g_i is the degeneracy of the state and μ is the chemical potential. With the conservation of particles, it is required that:

$$\begin{aligned} N &= \sum_{\substack{i=0\\(levels)}}^{\infty} N_i^* = \sum_{\substack{i=0\\(levels)}}^{\infty} \frac{g_i}{e^{\alpha+\beta\,\varepsilon_i}-1} = \frac{g_o}{e^{\alpha}e^{\beta\varepsilon_o}-1} + \frac{g_1}{e^{\alpha}e^{\beta\varepsilon_1}-1} + \cdots \\ &= N_o + N_1 + \cdots \end{aligned} \tag{2}$$

The summation in Eqn. (2) is sum over (energy) levels. Supposing we do a sum over states, then it is necessary that we give a statistical weight to each state. Since there is no restriction on the number of particles occupying a particular state, each state can be given a statistical weight of **1**. The condition $e^{-\beta\mu} \geq 1$, or $\mu \leq 0$, is required to have positive numbers of particles.

The maximum value of α. As the total number of particles in the ground state, i.e. $\varepsilon_o = 0$, is $N_o = N$ we have

$$N_o = f(\varepsilon_o = 0) = \frac{1}{e^{\alpha}-1}\,,$$

then

$$N = \frac{1}{e^{\alpha}-1} \qquad \Rightarrow \quad \alpha = \ln\left(1+\frac{1}{N}\right) \approx \frac{1}{N}$$

As $N \to \infty$, we find $\alpha = 0$, or $e^{\alpha} = 1$

The number of particles in the excited states

Mathematical Description:

$$N_e = N = \sum_{\substack{i=0\\(levels)}}^{\infty} N_i^* = \int_0^{\infty} \frac{g(\varepsilon)d\varepsilon}{e^{\alpha}e^{\beta\,\varepsilon}-1} \quad . \tag{3}$$

Where $g(\varepsilon) = 2\left(\frac{V}{h^3}\right)\pi\left(2m\right)^{3/2}\sqrt{\varepsilon}$, with the spin factor = 1. Eqn (3) are often found expressions for a Bose ideal gas in texts.

$$\begin{aligned} N_e &= 2\left(\frac{V}{h^3}\right)\pi\left(2m\right)^{3/2}\int_0^{\infty}\frac{\sqrt{\varepsilon}\;d\varepsilon}{e^{\alpha+\beta\,\varepsilon}-1} = \frac{V}{\lambda^3}\frac{2}{\sqrt{\pi}}\underbrace{\int_0^{\infty}\frac{\sqrt{x}dx}{e^{\alpha}e^{x}-1}}_{1.306\sqrt{\pi}\text{ as } e^{\alpha}=1} \\ &= 2.612\,V\times\left(\frac{2\pi\,mk_BT}{h^2}\right)^{3/2} \end{aligned} \tag{4}$$

where $x = \beta\varepsilon$, and $\lambda = \frac{h}{\sqrt{2\pi\,mk_BT}}$ is the De-Broglie wavelength.

By incorporating the density of states $g(\varepsilon)$, no weight is given to $\varepsilon = 0$ state (zero momentum state) as the kinetic energy of the particles goes to zero in this energy level. In quantum mechanical treatment this is incorrect as the particles essentially occupy the lower energy states in the low temperature and high density limit where quantum effects become dominant. Hence it is necessary that we take this term out of the summation (Eqn. 2) before carrying out the integration.

For the density of states we have to revise it in the form:

$$g(\varepsilon) = \delta(\varepsilon) + \left(\frac{2\pi V}{h^3}\right)(2m)^{3/2}\sqrt{\varepsilon}\,, \qquad \delta(\varepsilon) = \text{Dirac's delta function}$$

Note that:

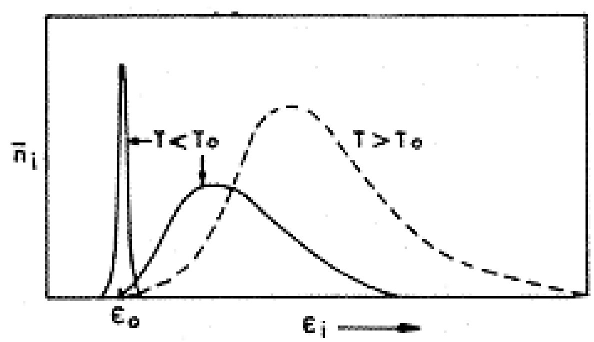
$$\int_{-\infty}^{\infty} f(x)\delta(x-a)dx = f(a) \Rightarrow \int_{-\infty}^{\infty} f(x)\delta(x)dx = f(0)$$

Then we have for the total number of particles:

$$N = \int_0^\infty d\varepsilon \frac{1}{z^{-1}e^{\beta\varepsilon} - 1}\left[\delta(\varepsilon) + \left(\frac{2\pi V}{h^3}\right)(2m)^{3/2}\varepsilon^{1/2}\right]$$

$$= \underbrace{\left(\frac{1}{e^{\alpha} - 1}\right)}_{N_o} + \underbrace{2\left(\frac{V}{h^3}\right)\pi(2m)^{3/2}\int_0^\infty d\varepsilon \frac{\varepsilon^{1/2}}{e^{\alpha}e^{\beta\varepsilon} - 1}}_{N_e} \qquad (5)$$

where N_e refers to the number of particles in the **excited states** and N_0 is the number of particles in the $\varepsilon = 0$ state.



Schematic diagram of the distribution function for the particles of an ideal BE gas.

When the temperature is very high (classical limit), then $e^{\beta\mu} << 1$ and μ is a –ve quantity. Under such conditions, the term $\left(e^{\alpha} - 1\right)^{-1}$ is well behaved and does not give a significant contribution to *N*. In other words $N_0 << N$ and N_e is large. Hence most particles are in the excited states and not in the $\varepsilon = 0$ state. But as the temperature approaches 0 K, $e^{\alpha} \to 1$ and the term $\left(e^{\alpha} - 1\right)^{-1}$ diverges as $e^{\alpha} = 1$ at T = 0 K. The contribution from singularity terms becomes more significant under these conditions. Here N_0 becomes much more significant compared to N_e. Thus the $\varepsilon = 0$ level gets densely populated. This is what is called ***Bose-Einstein condensation***.

$$N_e = 2.612\,V \times \left(\frac{2\pi\, mk_B T}{h^2}\right)^{3/2} \tag{6}$$

As $N_e = N$, and $T = T_B$, we have

$$T_B = \frac{h^2}{2\pi\, mk_B}\left(\frac{\rho}{2.612}\right)^{2/3} \quad , \quad \rho = \frac{N}{V} \tag{7}$$

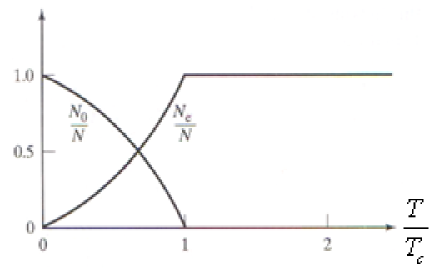
Dividing Eq. 6 by Eq. 7 gives the maximum number of particles occupying states above the ground state is

$$N_e = N\left(\frac{T}{T_B}\right)^{3/2} \qquad T > T_B \tag{8}$$

and the rest of the particles

$$N_o = N - N_e = N\left[1 - \left(\frac{T}{T_B}\right)^{3/2}\right] \qquad T < T_B \tag{9}$$

must condense into the ground state. This rapid increase in the population of the ground state below T_c is called Bose-Einstein condensation.



Example: For ^{4}He calculate T_B at 1 atm.

Answer: Use $N = N_A = 6.02\times10^{23}$ molecules/mol, $m = 4\times1.66\times10^{-27} = 6.65\times10^{-27}$ kg, and $V = 22.4\times10^{-3}$ m^3/mole, then

$$T_B = \frac{h^2}{2\pi\, mk_B}\left(\frac{N}{2.612\,V}\right)^{2/3}$$

$$= \frac{(6.63\times10^{-34})^2}{2\pi(6.65\times10^{-27})\times1.38\times10^{-23}}\left(\frac{6.02\times10^{23}}{2.612\times22.4\times10^{-3}}\right)^{2/3} = 0.036 \text{ K.}$$

It is small compared to the experimental value 4.21 K.

NOTES:

1. B.E. condensation can occur only when the particle number is conserved. For example, photon do not condense, they have a simpler alternative, namely, to disappear into the vacuum.
2. At $T < T_c$ the system may be looked upon as a mixture of two "phases"
   (a) A gaseous phase [N_e], particles distributed over the excited states ($\varepsilon \neq 0$), and
   (b) A condensed phase, consisting of [N_o] particles accumulated in the ground state ($\varepsilon = 0$).

18.4 Properties of a boson gas

The bosons in the ground state do not contribute to the internal energy nor to the heat capacity. The first term in the sum $\sum_i N_i \varepsilon_i$ is $N_0\varepsilon_0$. For $T < T_B$, N_0 may be large but ε_0 = 0, and for $T > T_B$, N_0 = 0 in any case.

Energy

For temperatures above the Bose temperature, all the bosons are in excited states and we may expect the internal energy to approach $(3/2)Nk_BT$ as the temperature is increased, i.e.

At high temperature $T > T_B$

$$U_+ \to \frac{3}{2} Nk_BT \qquad\qquad T > T_B$$

Below the Bose temperature the number of bosons in the excited states is $N_{ex} = N(T/T_B)^{3/2}$. As a first approximation, we assume that each of these bosons will have a thermal energy of the order of *kT*. Thus

$$U_- \approx Nk_BT\left(\frac{T}{T_B}\right)^{3/2} \qquad T < T_B$$

indicating that U_- varies as $T^{5/2}$ below the Bose temperature. A more nearly exact result is obtained by noting that the internal energy of the system is given by

$$U_- = \sum_i \varepsilon_i n_i^* = \int_0^\infty \varepsilon\, dn = \int_0^\infty \frac{\varepsilon g(\varepsilon) d\varepsilon}{e^{\alpha+\beta\varepsilon}-1} = \frac{V}{h^3} 2\pi(2m)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{\alpha+\beta\varepsilon}-1}$$

Use $x = \beta\varepsilon$, $e^\alpha = 1$, we have

$$U_- = \frac{2}{\sqrt{\pi}} k_BT\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2} V \underbrace{\int_0^\infty \frac{x^{3/2}dx}{e^x-1}}_{1.78}$$

Using

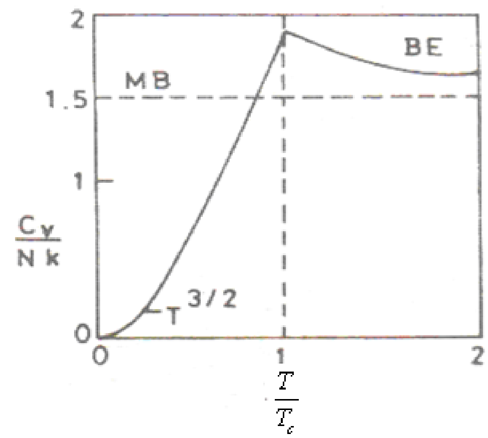
$$V = \frac{N}{2.612}\left(\frac{h^2}{2\pi\, mk_BT_B}\right)^{3/2}$$

We get

$$U_- = 0.77 Nk_BT\left(\frac{T}{T_B}\right)^{3/2},$$

not greatly different from our approximation.

In Summary: $U_- = 0.77 Nk_BT\left(\frac{T}{T_B}\right)^{3/2}$, $\quad U_+ \to \frac{3}{2} Nk_BT$



Specific heat

It is a simple matter now to obtain the heat capacity:

$$C_{V-} = \left(\frac{\partial U_-}{\partial T}\right)_V \approx 1.926\, N\, k_B \left(\frac{T}{T_B}\right)^{3/2} \quad ,$$

$$C_{V+} = \left(\frac{\partial U_+}{\partial T}\right)_V \approx \frac{3}{2} N k_B$$

At $T = T_c$, the values $C_{V+} = C_{V-} = 1.962 N k_B$

Entropy

$$S_-(T) = \int_0^T \frac{C_{V-}}{T'} dT' = \frac{2}{3} C_{V-} = 1.28\, N\, k_B \left(\frac{T}{T_B}\right)^{3/2} \quad ,$$

$$S_+(T) = S(T_B) + \int_{T_B}^{T} \frac{C_{V+}}{T'} dT = S(T_B) + \frac{3}{2} N\, k_B \left[\ln\left(\frac{T}{T_B}\right) + \cdots\right]$$

The entropy shows sudden drop for $T < T_B$. In $S_-(T)$, $S = 0$ at $T = 0$, accordance with the third law of thermodynamics. This means that for the condensed phase (which exist at $T = 0$) the entropy is zero, that is, all the particles are in one state.

Pressure

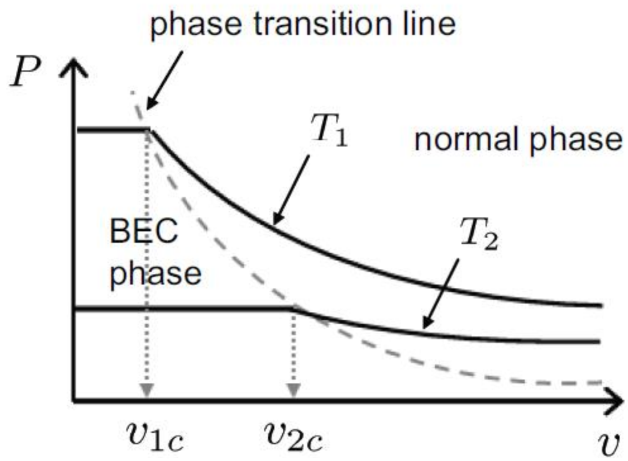
For ideal gases in three dimensions, the thermodynamic relation $P = \frac{2}{3} u$ is hold, independently of the statistics.

Therefore using $\frac{V}{V_c} = \left(\frac{T}{T_B}\right)^{3/2}$, we have

$$P_- = \frac{2}{3} \frac{U_-}{V} = 0.51 \frac{N k_B T^{5/2}}{T_B^{3/2}} = 0.51 \frac{N k_B T}{V_B},$$

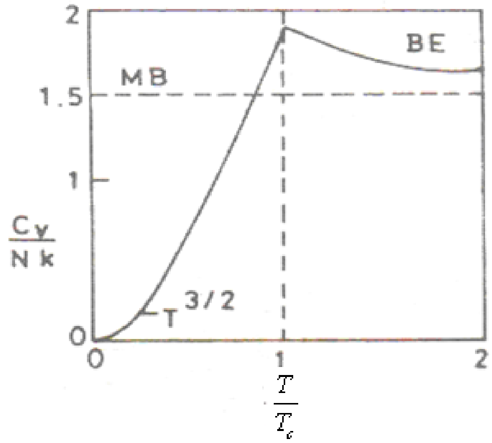
$$P_+ = \frac{2}{3} \frac{U_+}{V} = 0.51 \frac{N k_B T}{V} \left[1 - \cdots\right].$$

Note that: For $T < T_B$, P_- is independent on *V* and a function of *T* only, as for a condensing gas. The pressure of the gas does not depend on the volume in a BEC regime so that the compressibility of the BEC phase is infinite. This pathological feature is remedied by the inclusion of the two-body interactions. The following figure shows the equation of state of the ideal Bose gas.

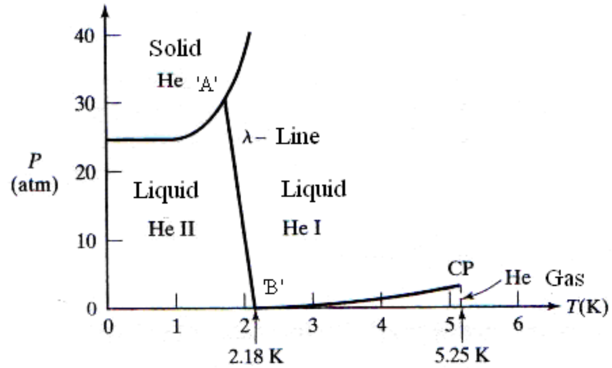


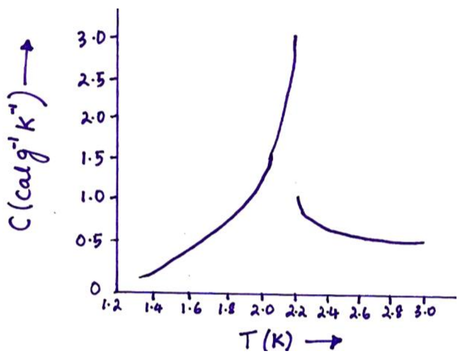
Pressure of the ideal Bose gas vs the specific volume $v = V / N$ for two temperatures $T_1 > T_2$.

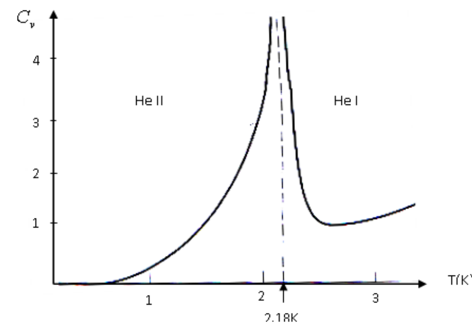
This is due to the fact that, when compressing a degenerate Bose gas, we just force more particles to occupy the ground state. ***The particles in the ground state do not contribute to pressure*** – except of the zero-motion oscillations, they are at rest.

Physical quantity	$T > T_B$	$T < T_B$
Internal energy (U)	$U_+ \to \frac{3}{2} N k_B T$	$U_- = 0.77 N k_B T \left(\frac{T}{T_B}\right)^{3/2}$
Specific heat (C_V)	$C_{V+} = \left(\frac{\partial U_+}{\partial T}\right)_V \approx \frac{3}{2} N k_B$	$C_{V-} = \left(\frac{\partial U_-}{\partial T}\right)_V \approx 1.92\, N\, k_B \left(\frac{T}{T_B}\right)^{3/2}$
		
Entropy (S)	$S_+(T) = S(T_B) + \frac{3}{2} N\, k_B \left[\ln\left(\frac{T}{T_B}\right) + \cdots \right]$	$S_- = \int_0^T \frac{C_{V-}}{T'} dT' = 1.28\, N\, k_B \left(\frac{T}{T_B}\right)^{3/2}$
Helmholtz free energy (F)		$F_- = U_- - TS_- = -1.33\; k_B T \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$
Pressure (P)	$P_+ = \frac{2}{3}\frac{U_+}{V} = 0.51 \frac{N k_B T}{V} [1 - \cdots]$	$P_- = -\left(\frac{\partial F_-}{\partial V}\right)_{T,N} = 1.33\; k_B T \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$

An experimental evidence for Bose–Einstein condensation came from the (C_V, T) relationship of ^4He. Phase transition of ^4He was found to occur at 2.19 K. When the mass, $m = 4 \times 1.66 \times 10^{-27} = 6.65 \times 10^{-27}$ kg and volume, $V = 27.6\ \text{cm}^3/\text{mole}$ the transition temperature it was found to be 3.13. The two numbers were not drastically different and the similarity between the (C_V vs. T) plot of an ideal Bose gas and that of ^4He was enough evidence to prove that the phase transition in ^4He is actually Bose-Einstein condensation.







Struck by the shape of this graph, the phase transition was given the name $\lambda-$transition and the transition point was called $\lambda-$transition point.

There are several applications of BEC in actual research.

1- One interesting application is the matter waves produced coherently by BEC, or atom laser. The beam is made of atomic waves and has special interest in any experiment that uses an atomic beam since the coherency can improve the precision of some measurements such as in atomic clocks.

2- Another interesting experiment is the production of a vortex lattices in the BEC media. This is especially interesting since the superfluidity property do not allow a vortex formation when the media is "stirring up". However, when one spin the trap of a dilute gas BEC the formation of several "local" vortices appear. The combination of this technique with a optical lattice formation tends to be promising in order to study also superconductors.

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(* I used N kB =1, Tc = 1, r = T *)
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UP[r_] := If[$r \le 1$, $0.77\, r^{5/2}$, $1.5\, r\left(1 - 0.463\,\frac{1}{r^{3/2}} - 0.023\,\frac{1}{r^3}\right)$]

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Plot[UP[r], {r, 0, 2}]
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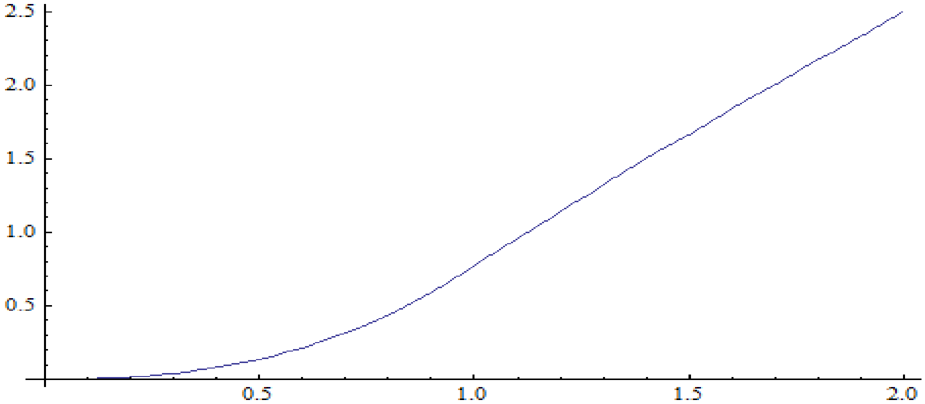

Cv[r_] := If[$r \le 1$, $1.926\, r^{3/2}$, $1.5\left(1 + 0.231\,\frac{1}{r^{3/2}} + 0.045\,\frac{1}{r^3}\right)$]

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Plot[Cv[r], {r, 0, 3}]
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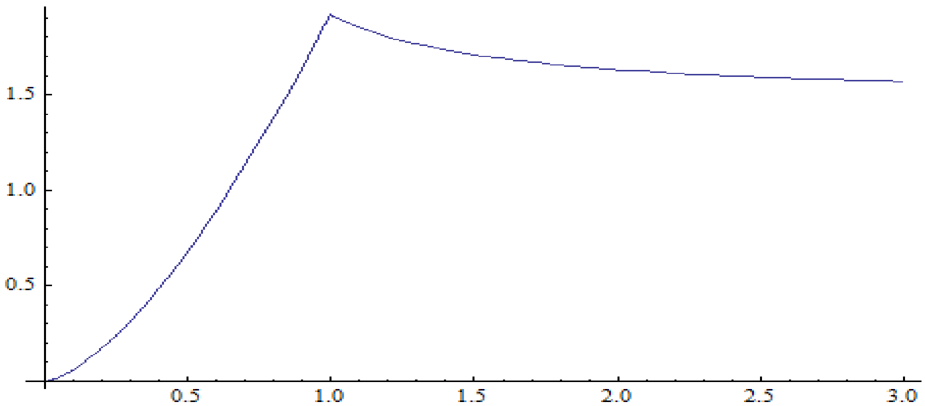

Sv[r_] := If[$r \le 1$, $1.28\, r^{3/2}$, Sv[1] + $1.5\left(\text{Log}[r] + 0.3465\left(1 - \frac{1}{r}\right)^{3/2}\right)$]

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Plot[Sv[r], {r, 0, 2}]
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