General Assumptions

These are some general assumptions, the validity of which is required to generate a meaningful solution.

```
$Assumptions = {E > 0, ℏ > 0, m > 0, L > 0, k > 0, T > 0, R > 0, s > 0};
```

Description of the problem

In quantum mechanics, we usually aim at solving Schrödinger's equation:
$\hat{H}\Psi = E\,\Psi$,

where $\hat{H}$ is the Hamiltonian operator (assigned to energy), Ψ is the so-called wave function, and E is the value of energy.

One convenient way of writing out $\hat{H}$ is to assume that

$\hat{H} = \hat{T} + \hat{V}$,

that is, a sum of kinetic ($\hat{T}$) and potential energy ($\hat{V}$) operators.

While for most systems

$\hat{T} = -\frac{\hbar^2}{2\,m}\,\frac{\partial^2}{\partial x^2}$,

definition of the potential energy depends on the interactions within the system. In case of a ***particle in a box***, we usually assume that

$\hat{V} = 0$ if $0 < x < L$ (where L is the length of the box), otherwise $\hat{V} = \infty$.

Solution of Schrödinger's Equation

Let us first solve the 2nd order ODE by specifying two boundary conditions:

```
solution[x_] = FullSimplify[Ψ[x] /. ReplaceAll[
    First@DSolve[-ℏ^2/(2 m) D[Ψ[x], {x, 2}] == E Ψ[x], Ψ[x], x], {C[1] → A, C[2] → B}]];
Print["Ψ(x) = ", solution[
  x]]
```

$\Psi(x) = A\,\mathrm{Cos}\left[\frac{\sqrt{2}\,x\,\sqrt{m\,E}}{\hbar}\right] + B\,\mathrm{Sin}\left[\frac{\sqrt{2}\,x\,\sqrt{m\,E}}{\hbar}\right]$

Note that this is a family of functions, where A and B could, in principle, take any values. We are only concerned with cases in which $\Psi(0) = \Psi(L) = 0$. Thus let us solve the following set of equations:

```
Reduce[{
  solution[0] == 0,
  solution[L] == 0
 }, {A, B}]
```

$$\left(\text{Sin}\left[\frac{\sqrt{2}\,L\sqrt{m\,E}}{\hbar}\right] == 0\ \&\&\ A == 0\right)\ ||\ \left(A == 0\ \&\&\ \text{Sin}\left[\frac{\sqrt{2}\,L\sqrt{m\,E}}{\hbar}\right] \neq 0\ \&\&\ B == 0\right)$$

From the above two conditions, only the first one is physically meaningful. Thus, $A = 0$ and we have a constraint on the value of E:

```
A = 0;
E = E /. Solve[√2 L √(m E)/ℏ == n π, E][[1]];
Print["E = ", E]
```

$$E = \frac{n^2\,\pi^2\,\hbar^2}{2\,L^2\,m}$$

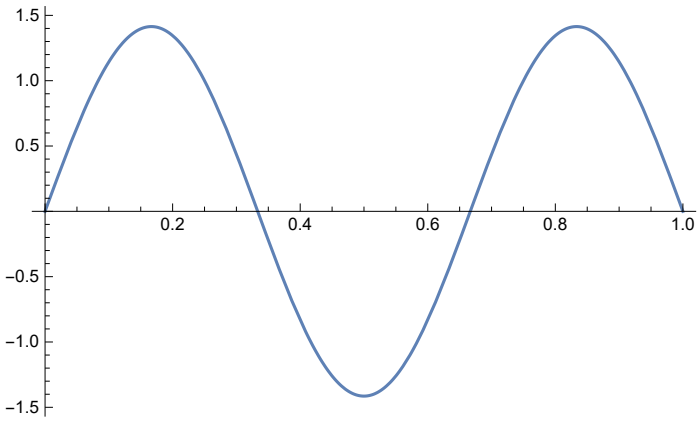
The value of B can be calculated by normalizing the squared wave function to 1:

```
B = B /. FullSimplify[Solve[Integrate[solution[x]^2, {x, 0, L}] == 1, B],
      Assumptions → {n ∈ Integers}][[2]];
Print[
 "B
   =
   ", B]
```

$$B = \frac{\sqrt{2}}{\sqrt{L}}$$

We can now do some test plotting:

```
L = 1;
ℏ = 1;
n = 3;
Plot[solution[x], {x, 0, L}]
```




```
Quit[];
```

Finding the fundamental equation

Let us start with the previously obtained energy expression:

```
En =n^2 π^2 ℏ^2/(2 L^2 m);
```

The probability of a given energy state to be filled is proportional to $\mathrm{Exp}\left[-\frac{\mathrm{En}}{\mathrm{k\,T}}\right]$. Sum these up (that is, integrate) to get the sum of probabilities for one molecule:

```
Ωmol = ReplaceAll[(Integrate[Exp[-En/(k T)], {n, 0, ∞}])^3, {L^3 → v}]
```

$$\frac{(\mathrm{M\,R\,T})^{3/2}\,\mathrm{v}}{2\sqrt{2}\,\mathrm{NA}^3\,\pi^{3/2}\,\hbar^3}$$

The number of possible states for all molecules of 1 mole of the system is thus $\Omega = \frac{1}{\mathrm{NA}!}\,\Omega\mathrm{mol}^{\mathrm{NA}}$, from which:

```
Smolar = k (NA Log[Ωmol] - NA Log[NA] + k NA);
Smolar = R (Log[Ωmol] - Log[NA] + 1)
```

$$\mathrm{R}\left(1-\mathrm{Log}[\mathrm{NA}]+\mathrm{Log}\left[\frac{(\mathrm{M\,R\,T})^{3/2}\,\mathrm{v}}{2\sqrt{2}\,\mathrm{NA}^3\,\pi^{3/2}\,\hbar^3}\right]\right)$$

Note that this is in fact the molar entropy. Rearrange this to express *T* as a function of the molar entropy *s*:

```
T /. Solve[Smolar == s, T][[1]]
```

$$\frac{2\,e^{-\frac{2}{3}+\frac{2\,s}{3\,R}}\,\mathrm{NA}^{8/3}\,\pi\,\hbar^2}{\mathrm{M\,R\,v}^{2/3}}$$

Integrate to get the molar internal energy *u*:

```
u = Integrate[%, s];
k = R / NA;
m = M / NA;
u = FullSimplify[u]
```

$$\frac{3\,e^{\frac{2}{3}\left(-1+\frac{s}{R}\right)}\,\mathrm{NA}^{8/3}\,\pi\,\hbar^2}{\mathrm{M\,v}^{2/3}}$$

Multiply by *n* to get the internal energy *U,* solve for *s*, switch to extensive variables:

```
s /. FullSimplify[Solve[U == n u, s], Assumptions → {C[1] == 0}][[1]];
FullSimplify[n ReplaceAll[%, {v → V / n }], Assumptions → {n > 0}]
```

$$\mathrm{n}\left(\mathrm{R}-\frac{3}{2}\,\mathrm{R}\,\mathrm{Log}\left[\frac{3\,\mathrm{n}^{5/3}\,\mathrm{NA}^{8/3}\,\pi\,\hbar^2}{\mathrm{M\,U\,V}^{2/3}}\right]\right)$$