Two-level system

In[22]:= `q[g0_, g1_, θ_, T_] = g0 + g1 Exp[-θ / T]`

Out[22]= $g0 + e^{-\frac{\theta}{T}}\, g1$

In[23]:= $U[g0\_, g1\_, \theta\_, T\_] = 8.3145 \dfrac{T^2}{q[g0, g1, \theta, T]} D[q[g0, g1, \theta, T], T]$

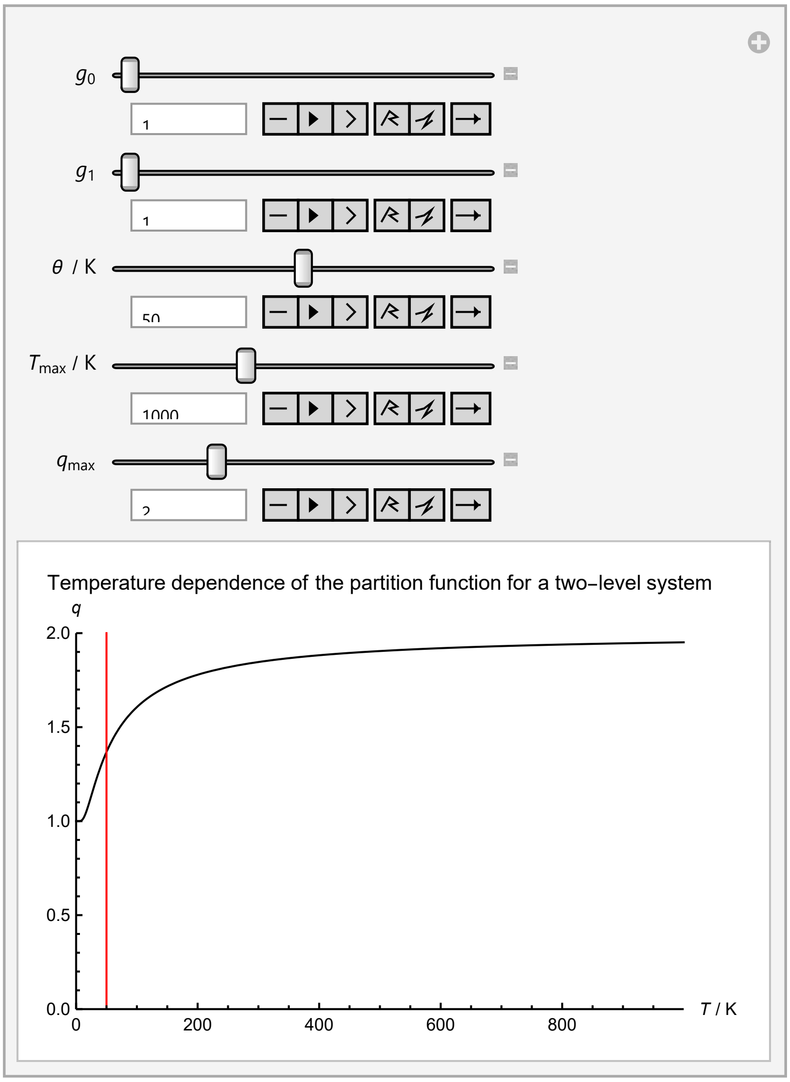
Out[23]= $$\frac{8.3145\, e^{-\frac{\theta}{T}}\, g1\, \theta}{g0 + e^{-\frac{\theta}{T}}\, g1}$$

In[24]:= `Cv[g0_, g1_, θ_, T_] = D[U[g0, g1, θ, T], T]`

Out[24]= $$-\frac{8.3145\, e^{-\frac{2\theta}{T}}\, g1^2\, \theta^2}{\left(g0 + e^{-\frac{\theta}{T}}\, g1\right)^2 T^2} + \frac{8.3145\, e^{-\frac{\theta}{T}}\, g1\, \theta^2}{\left(g0 + e^{-\frac{\theta}{T}}\, g1\right) T^2}$$

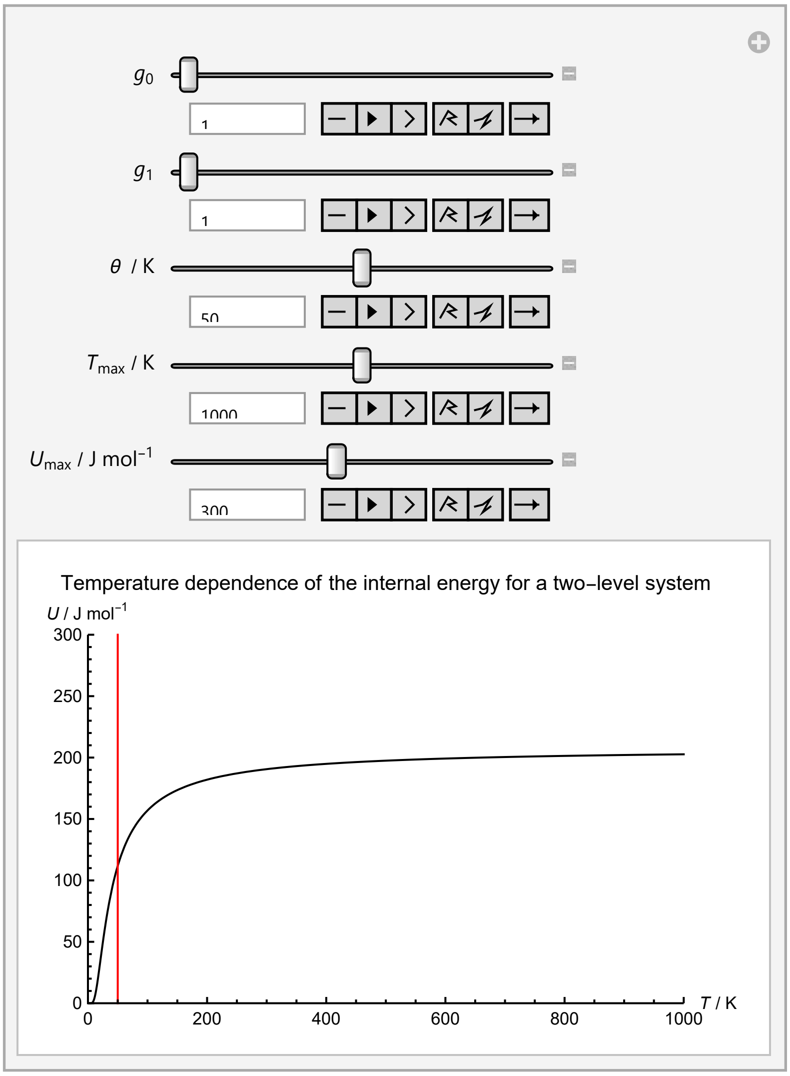
In[25]:=
```
Manipulate[Show[Plot[q[g0, g1, θ, T], {T, 0, Tmax}, PlotRange → {{0, Tmax}, {0, qmax}},
    AxesLabel → {"T / K", "q"}, PlotStyle → {{Black, AbsoluteThickness[1]}}, PlotLabel →
     "Temperature dependence of the partition function for a two-level system"],
   Graphics[{Red, Line[{{θ, 0}, {θ, qmax}}]}]], {{g0, 1, "g₀"}, 1, 4, 1},
  {{g1, 1, "g₁"}, 1, 4, 1}, {{θ, 50, "θ / K"}, 0, 100},
  {{Tmax, 1000, "Tmax / K"}, 0, 3000}, {{qmax, 2, "qmax"}, 0, 8}]
```

Out[25]=

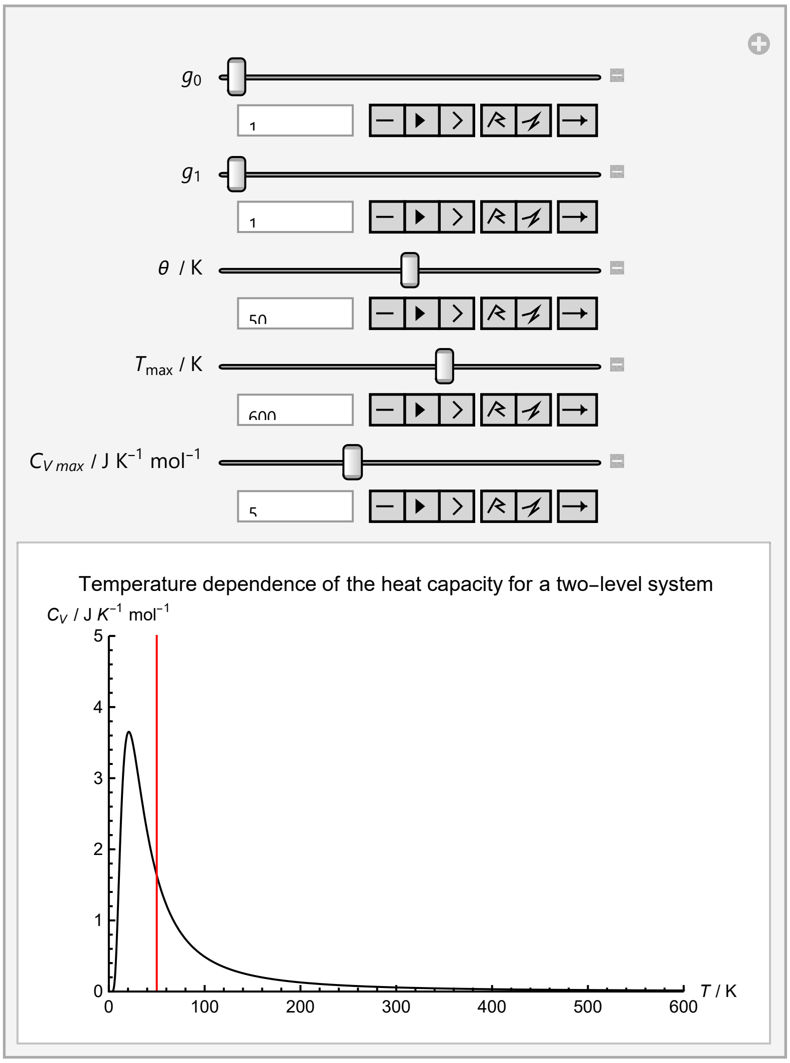


In[26]:=
```
Manipulate[Show[Plot[U[g0, g1, θ, T], {T, 0, Tmax},
    PlotRange → {{0, Tmax}, {0, Umax}}, AxesLabel → {"T / K", "U / J mol⁻¹"},
    PlotStyle → {{Black, AbsoluteThickness[1]}}, PlotLabel →
     "Temperature dependence of the internal energy for a two-level system"],
   Graphics[{Red, Line[{{θ, 0}, {θ, Umax}}]}]], {{g0, 1, "g₀"}, 1, 4, 1},
  {{g1, 1, "g₁"}, 1, 4, 1}, {{θ, 50, "θ / K"}, 0, 100},
  {{Tmax, 1000, "Tmax / K"}, 0, 2000},
  {{Umax, 300, "Umax / J mol⁻¹"}, 0, 700}]
```

Out[26]=



In[27]:=
```
Manipulate[Show[Plot[Cv[g0, g1, θ, T], {T, 0, Tmax},
    PlotRange → {{0, Tmax}, {0, Cvmax}}, AxesLabel → {"T / K", "CV / J K-1 mol-1"},
    PlotStyle → {{Black, AbsoluteThickness[1]}},
    PlotLabel → "Temperature dependence of the heat capacity for a two-level system"],
   Graphics[{Red, Line[{{θ, 0}, {θ, Cvmax}}]}]], {{g0, 1, "g0"}, 1, 4, 1},
  {{g1, 1, "g1"}, 1, 4, 1}, {{θ, 50, "θ / K"}, 0, 100},
  {{Tmax, 600, "Tmax / K"}, 0, 1000}, {{Cvmax, 5, "CV max / J K-1 mol-1"}, 0, 15}]
```

Out[27]=


Multi-level system

In[28]:= $q'[\theta\_, T\_] = \frac{1}{1 - \text{Exp}\left[\frac{-\theta}{T}\right]}$

Out[28]= $$\frac{1}{1 - e^{-\frac{\theta}{T}}}$$

In[29]:= `U'[θ_, T_] = 8.3145 T^2/q'[θ, T] D[q'[θ, T], T]`

$$\text{Out[29]=}\quad \frac{8.3145\, e^{-\frac{\theta}{T}}\, \theta}{1 - e^{-\frac{\theta}{T}}}$$

In[30]:= `Cv'[θ_, T_] = D[U'[θ, T], T]`

$$\text{Out[30]=}\quad \frac{8.3145\, e^{-\frac{2\theta}{T}}\, \theta^2}{\left(1 - e^{-\frac{\theta}{T}}\right)^2 T^2} + \frac{8.3145\, e^{-\frac{\theta}{T}}\, \theta^2}{\left(1 - e^{-\frac{\theta}{T}}\right) T^2}$$

In[31]:= `qlim[θ_, T_] = T / θ`

$$\text{Out[31]=}\quad \frac{T}{\theta}$$

In[32]:= `Ulim[θ_, T_] = 8.3145 T`

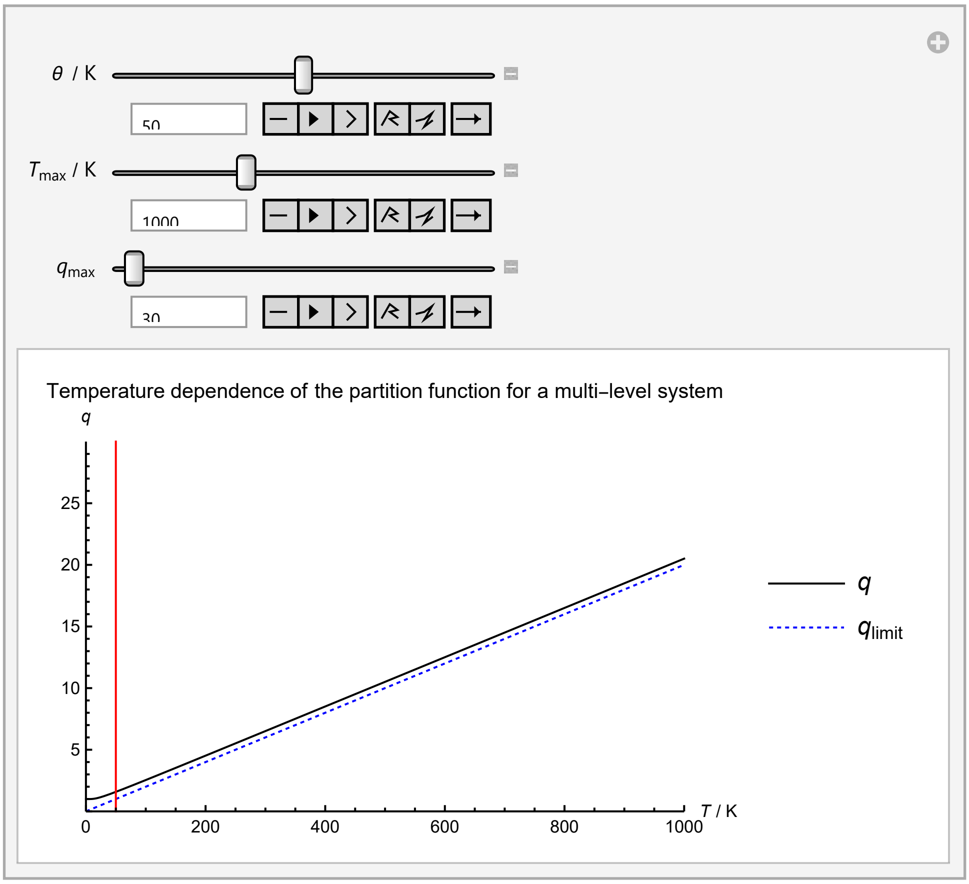
Out[32]= 8.3145 T

In[33]:= `Cvlim[θ_, T_] = 8.3145`

Out[33]= 8.3145

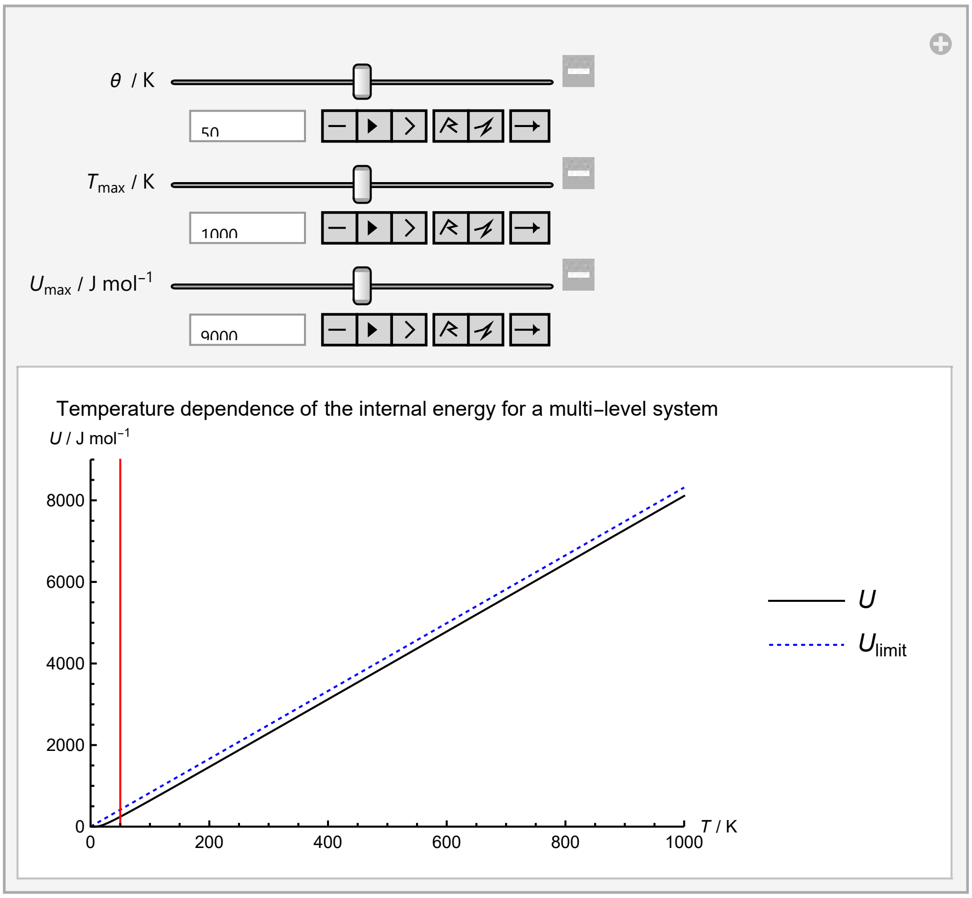
In[34]:=
```
Manipulate[
 Show[Plot[{q'[θ, T], qlim[θ, T]}, {T, 0, Tmax}, PlotRange → {{0, Tmax}, {0, qmax}},
   AxesLabel → {"T / K", "q"}, PlotStyle → {{Black, AbsoluteThickness[1]},
     {Blue, AbsoluteThickness[1], AbsoluteDashing[2]}}, PlotLabel →
    "Temperature dependence of the partition function for a multi-level system",
   PlotLegends → {"q", "qlimit"}], Graphics[{Red, Line[{{θ, 0}, {θ, qmax}}]}]],
 {{θ, 50, "θ / K"}, 0, 100}, {{Tmax, 1000, "Tmax / K"}, 0, 3000},
 {{qmax, 30, "qmax"}, 0, 3000}]
```

Out[34]=



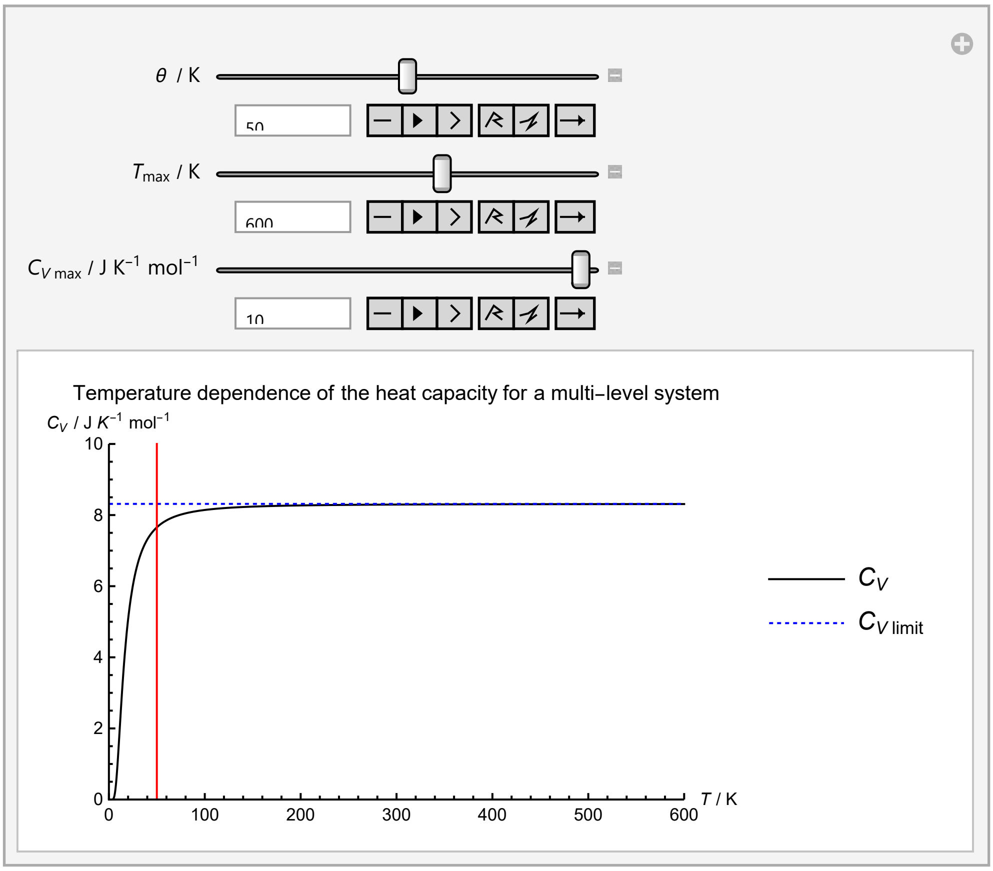
In[35]:=
```
Manipulate[
 Show[Plot[{U'[θ, T], Ulim[θ, T]}, {T, 0, Tmax}, PlotRange → {{0, Tmax}, {0, Umax}},
   AxesLabel → {"T / K", "U / J mol^-1"}, PlotStyle → {{Black, AbsoluteThickness[1]},
     {Blue, AbsoluteThickness[1], AbsoluteDashing[2]}}, PlotLabel →
    "Temperature dependence of the internal energy for a multi-level system",
   PlotLegends → {"U", "U_limit"}], Graphics[{Red, Line[{{θ, 0}, {θ, Umax}}]}]],
 {{θ, 50, "θ / K"}, 0, 100}, {{Tmax, 1000, "T_max / K"}, 0, 2000},
 {{Umax, 9000, "U_max / J mol^-1"}, 0, 18000}]
```

Out[35]=



In[36]:=
```
Manipulate[
 Show[Plot[{Cv'[θ, T], Cvlim[θ, T]}, {T, 0, Tmax}, PlotRange → {{0, Tmax}, {0, Cvmax}},
   AxesLabel → {"T / K", "CV / J K^-1 mol^-1"}, PlotStyle →
    {{Black, AbsoluteThickness[1]}, {Blue, AbsoluteThickness[1], AbsoluteDashing[2]}},
   PlotLabel → "Temperature dependence of the heat capacity for a multi-level system",
   PlotLegends → {"CV", "CV limit"}], Graphics[{Red, Line[{{θ, 0}, {θ, Cvmax}}]}]],
 {{θ, 50, "θ  / K"}, 0, 100}, {{Tmax, 600, "Tmax / K"}, 0, 1000},
 {{Cvmax, 10, "CV max / J K^-1 mol^-1"}, 0, 10}]
```

Out[36]=



Questions

1.

T << θ:

- q tends to g0, only lower level occupied
- U tends to 0, lower level has zero energy
- Cv tends to 0, higher energy level is too high to occupy

T >> θ:

- q tends to g0+g1, spacing of levels is much smaller than kT so they are equally occupied
- U tends to a maximum, levels equally occupied, value depends on g1:g0
- Cv tends to 0, no further levels to occupy

2.

T << θ:
- q tends to 1, only lower level occupied
- U tends to 0, lower level has zero energy
- Cv tends to 0, higher energy level is too high to occupy

T >> θ:
- q increases linearly, infinite levels with spacing < kT
- U increases linearly, higher and higher levels can be occupied at higher temperatures, approaching equipartition principle
- Cv tends to R, spacing much lower than kT, approaching equipartition principle

3.
q and U:
- Two-level system has a rapid increase approaching T = θ, followed by a plateau at T > θ, whilst multi-level system increases gradually to T = θ, followed by steeper linear increase at T > θ. Due to finite nature of two-level system - there is a limit on the internal energy.

Cv:
- Two-level system tends to zero at both low and high temperatures, whilst multi-level system rises rapidly to T = θ, followed by a plateau at T > θ. Due to the multi-level system internal energy increasing at a constant rate as more levels become occupied.