

Problem 6.21

Problem 6.21. In the real world, most oscillators are not perfectly harmonic. For a quantum oscillator, this means that the spacing between energy levels is not exactly uniform. The vibrational levels of an H_2 molecule, for example, are more accurately described by the approximate formula

$$E_n \approx \epsilon(1.03n - 0.03n^2), \quad n = 0, 1, 2, \dots,$$

where ϵ is the spacing between the two lowest levels. Thus, the levels get closer together with increasing energy. (This formula is reasonably accurate only up to about $n = 15$; for slightly higher n it would say that E_n decreases with increasing n . In fact, the molecule dissociates and there are no more discrete levels beyond $n \approx 15$.) Use a computer to calculate the partition function, average energy, and heat capacity of a system with this set of energy levels. Include all levels through $n = 15$, but check to see how the results change when you include fewer levels. Plot the heat capacity as a function of kT/ϵ . Compare to the case of a perfectly harmonic oscillator with evenly spaced levels, and also to the vibrational portion of the graph in Figure 1.13.

First, here is a way to use Mathematica's symbolic evaluations to work with the partition function. Consider a very simple two-term partition function with energy levels ϵ_1 and ϵ_2 :

```
In[1]:= Z = Exp[-β ε1] + Exp[-β ε2]
```

The average value of the energy is calculated symbolically by:

```
In[2]:= Ebar = -1/Z D[Z, β]
```

You can express that as a function of temperature T by using a replacement rule, replacing β by $1/(k T)$.

```
In[3]:= EbarT[T_] = Ebar /. β → 1 / (k T)
```

Then the heat capacity is the derivative of the energy with respect to the temperature.

```
In[9]:= c = D[EbarT[T], T]
```

This is quite complicated, but can be simplified:

```
In[10]:= Simplify[%]
```

Try it all again with a more complicated partition function

```
In[51]:= Clear[Z, Ebar, EbarT, c]
```

```
In[52]:= En[n_] := ε (1.03 n - 0.03 n^2)
```

In[63]:= **Z15 = Sum[Exp[-β En[n]], {n, 1, 15}]**

Out[63]=

$$e^{-8.7\beta\epsilon} + e^{-8.54\beta\epsilon} + e^{-8.32\beta\epsilon} + e^{-8.04\beta\epsilon} + e^{-7.7\beta\epsilon} + e^{-7.3\beta\epsilon} + e^{-6.84\beta\epsilon} + e^{-6.32\beta\epsilon} + e^{-5.74\beta\epsilon} + e^{-5.1\beta\epsilon} + e^{-4.4\beta\epsilon} + e^{-3.64\beta\epsilon} + e^{-2.82\beta\epsilon} + e^{-1.94\beta\epsilon} + e^{-1.\beta\epsilon}$$

In[64]:= **Ebar15 = $\frac{-1}{Z15}$ D[Z15, β]**

Out[64]=

$$-\left((-8.7 e^{-8.7\beta\epsilon} - 8.54 e^{-8.54\beta\epsilon} - 8.32 e^{-8.32\beta\epsilon} - 8.04 e^{-8.04\beta\epsilon} - 7.7 e^{-7.7\beta\epsilon} - 7.3 e^{-7.3\beta\epsilon} - 6.84 e^{-6.84\beta\epsilon} - 6.32 e^{-6.32\beta\epsilon} - 5.74 e^{-5.74\beta\epsilon} - 5.1 e^{-5.1\beta\epsilon} - 4.4 e^{-4.4\beta\epsilon} - 3.64 e^{-3.64\beta\epsilon} - 2.82 e^{-2.82\beta\epsilon} - 1.94 e^{-1.94\beta\epsilon} - 1. e^{-1.\beta\epsilon}) / (e^{-8.7\beta\epsilon} + e^{-8.54\beta\epsilon} + e^{-8.32\beta\epsilon} + e^{-8.04\beta\epsilon} + e^{-7.7\beta\epsilon} + e^{-7.3\beta\epsilon} + e^{-6.84\beta\epsilon} + e^{-6.32\beta\epsilon} + e^{-5.74\beta\epsilon} + e^{-5.1\beta\epsilon} + e^{-4.4\beta\epsilon} + e^{-3.64\beta\epsilon} + e^{-2.82\beta\epsilon} + e^{-1.94\beta\epsilon} + e^{-1.\beta\epsilon}) \right)$$

In[65]:= **EbarT15[T_] = Ebar15 /. β → 1 / (k T)**

Out[65]=

$$-\left(\left(-8.7 e^{-\frac{8.7\epsilon}{kT}} - 8.54 e^{-\frac{8.54\epsilon}{kT}} - 8.32 e^{-\frac{8.32\epsilon}{kT}} - 8.04 e^{-\frac{8.04\epsilon}{kT}} - 7.7 e^{-\frac{7.7\epsilon}{kT}} - 7.3 e^{-\frac{7.3\epsilon}{kT}} - 6.84 e^{-\frac{6.84\epsilon}{kT}} - 6.32 e^{-\frac{6.32\epsilon}{kT}} - 5.74 e^{-\frac{5.74\epsilon}{kT}} - 5.1 e^{-\frac{5.1\epsilon}{kT}} - 4.4 e^{-\frac{4.4\epsilon}{kT}} - 3.64 e^{-\frac{3.64\epsilon}{kT}} - 2.82 e^{-\frac{2.82\epsilon}{kT}} - 1.94 e^{-\frac{1.94\epsilon}{kT}} - 1. e^{-\frac{1.\epsilon}{kT}} \right) / \left(e^{-\frac{8.7\epsilon}{kT}} + e^{-\frac{8.54\epsilon}{kT}} + e^{-\frac{8.32\epsilon}{kT}} + e^{-\frac{8.04\epsilon}{kT}} + e^{-\frac{7.7\epsilon}{kT}} + e^{-\frac{7.3\epsilon}{kT}} + e^{-\frac{6.84\epsilon}{kT}} + e^{-\frac{6.32\epsilon}{kT}} + e^{-\frac{5.74\epsilon}{kT}} + e^{-\frac{5.1\epsilon}{kT}} + e^{-\frac{4.4\epsilon}{kT}} + e^{-\frac{3.64\epsilon}{kT}} + e^{-\frac{2.82\epsilon}{kT}} + e^{-\frac{1.94\epsilon}{kT}} + e^{-\frac{1.\epsilon}{kT}} \right) \right)$$

In[66]:= **c15[T_] = D[EbarT15[T], T]**

Out[66]=

$$\left(\begin{aligned} & -8.7 e^{-\frac{8.7 \text{ €}}{k T}} \text{ €} - 8.54 e^{-\frac{8.54 \text{ €}}{k T}} \text{ €} - 8.32 e^{-\frac{8.32 \text{ €}}{k T}} \text{ €} - 8.04 e^{-\frac{8.04 \text{ €}}{k T}} \text{ €} - 7.7 e^{-\frac{7.7 \text{ €}}{k T}} \text{ €} - \\ & 7.3 e^{-\frac{7.3 \text{ €}}{k T}} \text{ €} - 6.84 e^{-\frac{6.84 \text{ €}}{k T}} \text{ €} - 6.32 e^{-\frac{6.32 \text{ €}}{k T}} \text{ €} - 5.74 e^{-\frac{5.74 \text{ €}}{k T}} \text{ €} - 5.1 e^{-\frac{5.1 \text{ €}}{k T}} \text{ €} - \\ & 4.4 e^{-\frac{4.4 \text{ €}}{k T}} \text{ €} - 3.64 e^{-\frac{3.64 \text{ €}}{k T}} \text{ €} - 2.82 e^{-\frac{2.82 \text{ €}}{k T}} \text{ €} - 1.94 e^{-\frac{1.94 \text{ €}}{k T}} \text{ €} - 1. e^{-\frac{1. \text{ €}}{k T}} \text{ €} \end{aligned} \right) \\ \left(\begin{aligned} & \frac{8.7 e^{-\frac{8.7 \text{ €}}{k T}} \text{ €}}{k T^2} + \frac{8.54 e^{-\frac{8.54 \text{ €}}{k T}} \text{ €}}{k T^2} + \frac{8.32 e^{-\frac{8.32 \text{ €}}{k T}} \text{ €}}{k T^2} + \frac{8.04 e^{-\frac{8.04 \text{ €}}{k T}} \text{ €}}{k T^2} + \frac{7.7 e^{-\frac{7.7 \text{ €}}{k T}} \text{ €}}{k T^2} + \\ & \frac{7.3 e^{-\frac{7.3 \text{ €}}{k T}} \text{ €}}{k T^2} + \frac{6.84 e^{-\frac{6.84 \text{ €}}{k T}} \text{ €}}{k T^2} + \frac{6.32 e^{-\frac{6.32 \text{ €}}{k T}} \text{ €}}{k T^2} + \frac{5.74 e^{-\frac{5.74 \text{ €}}{k T}} \text{ €}}{k T^2} + \frac{5.1 e^{-\frac{5.1 \text{ €}}{k T}} \text{ €}}{k T^2} + \\ & \frac{4.4 e^{-\frac{4.4 \text{ €}}{k T}} \text{ €}}{k T^2} + \frac{3.64 e^{-\frac{3.64 \text{ €}}{k T}} \text{ €}}{k T^2} + \frac{2.82 e^{-\frac{2.82 \text{ €}}{k T}} \text{ €}}{k T^2} + \frac{1.94 e^{-\frac{1.94 \text{ €}}{k T}} \text{ €}}{k T^2} + \frac{1. e^{-\frac{1. \text{ €}}{k T}} \text{ €}}{k T^2} \end{aligned} \right) \Bigg) / \\ \left(\begin{aligned} & e^{-\frac{8.7 \text{ €}}{k T}} + e^{-\frac{8.54 \text{ €}}{k T}} + e^{-\frac{8.32 \text{ €}}{k T}} + e^{-\frac{8.04 \text{ €}}{k T}} + e^{-\frac{7.7 \text{ €}}{k T}} + e^{-\frac{7.3 \text{ €}}{k T}} + e^{-\frac{6.84 \text{ €}}{k T}} + e^{-\frac{6.32 \text{ €}}{k T}} + e^{-\frac{5.74 \text{ €}}{k T}} + \\ & e^{-\frac{5.1 \text{ €}}{k T}} + e^{-\frac{4.4 \text{ €}}{k T}} + e^{-\frac{3.64 \text{ €}}{k T}} + e^{-\frac{2.82 \text{ €}}{k T}} + e^{-\frac{1.94 \text{ €}}{k T}} + e^{-\frac{1. \text{ €}}{k T}} \end{aligned} \right)^2 - \\ \left(\begin{aligned} & -\frac{75.69 e^{-\frac{8.7 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \frac{72.9316 e^{-\frac{8.54 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \frac{69.2224 e^{-\frac{8.32 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \frac{64.6416 e^{-\frac{8.04 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \\ & \frac{59.29 e^{-\frac{7.7 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \frac{53.29 e^{-\frac{7.3 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \frac{46.7856 e^{-\frac{6.84 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \\ & \frac{39.9424 e^{-\frac{6.32 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \frac{32.9476 e^{-\frac{5.74 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \frac{26.01 e^{-\frac{5.1 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \frac{19.36 e^{-\frac{4.4 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \\ & \frac{13.2496 e^{-\frac{3.64 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \frac{7.9524 e^{-\frac{2.82 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \frac{3.7636 e^{-\frac{1.94 \text{ €}}{k T}} \text{ €}^2}{k T^2} - \frac{1. e^{-\frac{1. \text{ €}}{k T}} \text{ €}^2}{k T^2} \end{aligned} \right) \Bigg) / \\ \left(\begin{aligned} & e^{-\frac{8.7 \text{ €}}{k T}} + e^{-\frac{8.54 \text{ €}}{k T}} + e^{-\frac{8.32 \text{ €}}{k T}} + e^{-\frac{8.04 \text{ €}}{k T}} + e^{-\frac{7.7 \text{ €}}{k T}} + e^{-\frac{7.3 \text{ €}}{k T}} + e^{-\frac{6.84 \text{ €}}{k T}} + e^{-\frac{6.32 \text{ €}}{k T}} + \\ & e^{-\frac{5.74 \text{ €}}{k T}} + e^{-\frac{5.1 \text{ €}}{k T}} + e^{-\frac{4.4 \text{ €}}{k T}} + e^{-\frac{3.64 \text{ €}}{k T}} + e^{-\frac{2.82 \text{ €}}{k T}} + e^{-\frac{1.94 \text{ €}}{k T}} + e^{-\frac{1. \text{ €}}{k T}} \end{aligned} \right)$$

Calculate the heat capacity for a scaled temperature 't = k T / €', or T = € t / k.

c15[t_] := c15[€ t / K. It's messy, so try to simplify it. To get a dimensionless quantity, divide by 'k'.

In[67]:= **cs15[t_] := Simplify[c15[€ t / k] / k]**

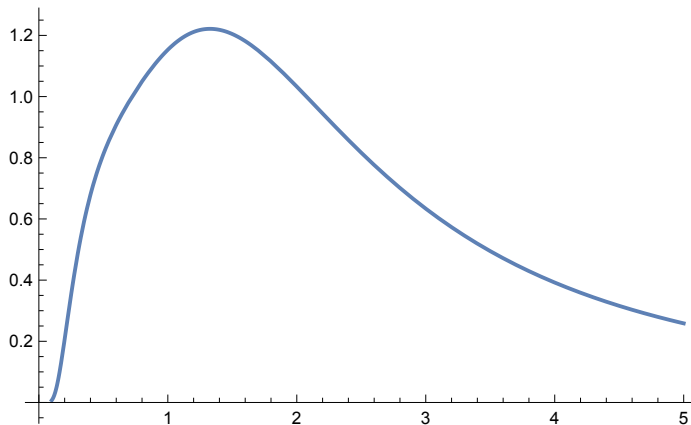
In[68]:= **cs15[t]**

Out[68]=

$$\begin{aligned}
& \left(75.69 e^{-172.8/t} \right. \\
& \quad \left(-1. \left(1. e^{77.7/t} + 0.981609 e^{77.86/t} + 0.956322 e^{78.08/t} + 0.924138 e^{78.36/t} + 0.885057 e^{78.7/t} + 0.83908 e^{79.1/t} + 0.786207 e^{79.56/t} + 0.726437 e^{80.08/t} + 0.65977 e^{80.66/t} + 0.586207 e^{81.3/t} + 0.505747 e^{82./t} + 0.418391 e^{82.76/t} + 0.324138 e^{83.58/t} + 0.222989 e^{84.46/t} + 0.114943 e^{85.4/t} \right) \right. \\
& \quad \left(1. e^{77.7/t} + 0.981609 e^{77.86/t} + 0.956322 e^{78.08/t} + 0.924138 e^{78.36/t} + 0.885057 e^{78.7/t} + 0.83908 e^{79.1/t} + 0.786207 e^{79.56/t} + 0.726437 e^{80.08/t} + 0.65977 e^{80.66/t} + 0.586207 e^{81.3/t} + 0.505747 e^{82./t} + 0.418391 e^{82.76/t} + 0.324138 e^{83.58/t} + 0.222989 e^{84.46/t} + 0.114943 e^{85.4/t} \right) + \\
& \quad 1. \left(1. e^{77.7/t} + 0.963557 e^{77.86/t} + 0.914551 e^{78.08/t} + 0.854031 e^{78.36/t} + 0.783327 e^{78.7/t} + 0.704056 e^{79.1/t} + 0.618121 e^{79.56/t} + 0.52771 e^{80.08/t} + 0.435297 e^{80.66/t} + 0.343639 e^{81.3/t} + 0.25578 e^{82./t} + 0.175051 e^{82.76/t} + 0.105065 e^{83.58/t} + 0.0497239 e^{84.46/t} + 0.0132118 e^{85.4/t} \right) \\
& \quad \left(e^{77.7/t} + e^{77.86/t} + e^{78.08/t} + e^{78.36/t} + e^{78.7/t} + e^{79.1/t} + e^{79.56/t} + e^{80.08/t} + e^{80.66/t} + e^{81.3/t} + e^{82./t} + e^{82.76/t} + e^{83.58/t} + e^{84.46/t} + e^{85.4/t} \right) \Big) \Big) / \\
& \quad \left(\left(e^{-8.7/t} + e^{-8.54/t} + e^{-8.32/t} + e^{-8.04/t} + e^{-7.7/t} + e^{-7.3/t} + e^{-6.84/t} + e^{-6.32/t} + e^{-5.74/t} + e^{-5.1/t} + e^{-4.4/t} + e^{-3.64/t} + e^{-2.82/t} + e^{-1.94/t} + e^{-1./t} \right)^2 t^2 \right)
\end{aligned}$$

In[71]:= **Plot[cs15[t], {t, 0.1, 5}, PlotRange → All]**

Out[71]=

In[50]:= **Clear["Global`*"]**