Question

The bond extension y of a vibrating diatomic molecule satisfies the differential equation

$$m\frac{d^2y}{dt^2} = -\frac{dV}{dy}$$

where m is the reduced mass and $V(y)$ is the potential energy. An approximation to $V(y)$ is given by the Morse potential:

$$Y(y) = d(1 - e^{-by})^2$$

where $d > 0$ and $b > 0$ are positive constants. Using the Morse potential $V(y)$:

(a) For what values of y does $V(y) = 0$? Find the turning points of V(y) and calculate $lim_{y\to-\infty}V(y)$ and $lim_{y\to-\infty}V(y)$. Sketch a ROUGH graph of V(y).

(b) Write down the Taylor series expansion for e^{-by} about $y = 0$. Hence shoe that when y is small the Morse potential is approximately

$$V(y) \approx d(by)^2.$$

(c) Using your approximation for V(y) when y is small, show that the molecule vibrates with a frequency

$$f = \frac{1}{2\pi}\sqrt{\frac{2db^2}{m}}.$$

Answer

(a)

$$\begin{aligned}
\text{Morse potential } V(y) &= d(1 - e^{-by})^2 \\
V(y) = 0 &\Leftrightarrow d(1 - e^{-by})^2 = 0 \\
&\Leftrightarrow (1 - e^{-by})^2 = 0 \\
&\Leftrightarrow e^{-by} = 1 \\
\text{since } b > 0, V(0) &= 0 \Leftrightarrow y = 0
\end{aligned}$$

Differentiating gives $\frac{dV}{dy} = 2d(1 - e^{-by})be^{-by}$

So turning points occur when $2d(1 - e^{-by})be^{-by} = 0$

This only happens when $(1 - e^{-by}) = 0$, and so when $y = 0$

There is only one turning point at y = 0.

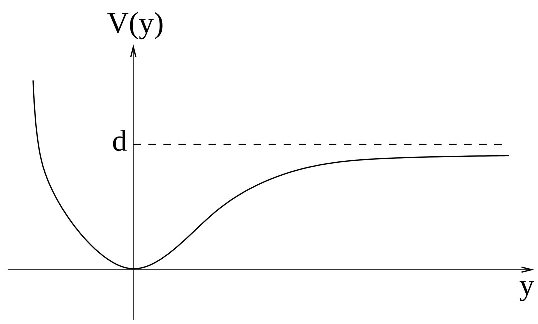
Nature of turning point: $\begin{cases} \frac{dV}{dy} < 0 \quad when \quad y < 0 \\ \frac{dV}{dy} > 0 \quad when \quad y > 0 \end{cases}$

So V(y) has a local minimum at y = 0.

As $y \to +\infty$, $e^{-by} \to 0$. So $\lim_{y \to +\infty} V(y) = d$

As $y \to -\infty$, $e^{-by} \to +\infty$. So $\lim_{y \to -\infty} V(y) = +\infty$

Graph of $V(y)$ against y:



Also see Figure 16.37 of (Figure 16.36 in the new edition)

P.W. Atkins, Physical Chemistry, Oxford, 1994.

(Copies at QA453 in the short loans section of the library.)

(b) Taylor expansion about $y = 0$:

$e^{-by} = 1 + (-by) + \frac{1}{2!}(-by)^2 + \frac{1}{3!}(-by)^3 + ...$

For small y, $e^{-by} \approx 1 - by$ (neglect terms of order 2 and above)

so for small y, $V(y) \approx d(1 - [1 - by])^2 = d(by)^2$

(c)

$$\begin{aligned} \text{Using approximation } V(y) &\approx d(by)^2 \\ \text{and } \frac{dV}{dy} &\approx 2db^2 y \end{aligned}$$

So the differential equation for the bond extension y becomes

$$m\frac{d^2y}{dt^2} = -2db^2 y \text{ or } m\frac{d^2y}{dt^2} + 2db^2 y = 0$$

which is the equation for simple harmonic motion. The auxiliary equation is

$$\lambda^2 + \frac{2db^2}{m} = 0$$

with a pair of complex conjugate roots $\lambda = \pm i\sqrt{\frac{2db^2}{m}}$

Hence the general solution is

$$y = A\cos\left(t\sqrt{\frac{2db^2}{m}}\right) + B\sin\left(t\sqrt{\frac{2db^2}{m}}\right)$$

Which is periodic with time period

$$T = \frac{2\pi}{\sqrt{\frac{2db^2}{m}}}$$

and frequency

$$f = \frac{1}{T} = \frac{1}{2\pi}\sqrt{\frac{2db^2}{m}}.$$