$$V = -\frac{1}{2}\mu^{2}(\pi^{2} + (v + \sigma)^{2}) + \frac{\lambda}{2}(\pi^{2} + (v + \sigma)^{2})^{2} - a(v + \sigma);$$

V /.
$$\left\{ v \rightarrow \frac{\mu}{\sqrt{\lambda}} + \frac{a}{2 \mu^2} \right\}$$
 // FullSimplify // Expand

$$\text{Out}[3] = \frac{\pi^4 \lambda}{4} + \frac{a^4 \lambda}{64 \, \mu^8} + \frac{a^3 \sqrt{\lambda}}{8 \, \mu^5} + \frac{a^2 \, \pi^2 \lambda}{8 \, \mu^4} - \frac{a^2}{4 \, \mu^2} + \frac{a \, \pi^2 \sqrt{\lambda}}{2 \, \mu} - \frac{a \, \mu}{\sqrt{\lambda}} - \frac{\mu^4}{4 \, \lambda} + \frac{a^3 \lambda \, \sigma}{8 \, \mu^6} + \frac{3 \, a^2 \sqrt{\lambda} \, \sigma}{4 \, \mu^3} + \frac{a \, \pi^2 \lambda \, \sigma}{4 \, \mu^3} + \frac{a \, \pi^2 \lambda \, \sigma}{2 \, \mu^2} + \frac{3 \, a^2 \lambda \, \sigma^2}{2 \, \mu^2} + \frac{3 \, a^2 \lambda \, \sigma^2}{2 \, \mu^2} + \frac{3 \, a^2 \lambda \, \sigma^2}{2 \, \mu^2} + \frac{3 \, a^2 \lambda \, \sigma^2}{2 \, \mu^2} + \frac{a \, \lambda \, \sigma^3}{2 \, \mu^2} + \sqrt{\lambda} \, \mu \, \sigma^3 + \frac{\lambda \, \sigma^4}{4}$$