Supplementary material

Non-linearity coefficient μ

1. The variation with pressure of the volume of a system for which μ is constant is given by $V(P)=V_0(1+aP)^{-\frac{1}{\mu}}$ where V_0 is a constant, which represents the volume of the system in the limit of vanishing pressure.

Since $\mu=-\left[\frac{\partial}{\partial P}\left(V\Big/\left(\frac{\partial V}{\partial P}\right)_T\right)\right]_T=V\left(\frac{\partial^2 V}{\partial P^2}\right)_T\Big/\left(\frac{\partial V}{\partial P}\right)_T^2-1$, an expression for $\mu(P)$ can easily be derived when the variation with pressure of the system volume is known as a power series $V(P)=\sum_{i=0}^{\infty}a_iP^i$: $\mu(P)=\sum_{i=0}^{\infty}a_iP^i\sum_{j=0}^{\infty}(j+1)(j+2)a_{j+2}P^j\Big/\sum_{i=0}^{\infty}(i+1)a_{i+1}P^i\sum_{j=0}^{\infty}(j+1)a_{j+1}P^j-1$

$$=\sum_{k=0}^{\infty}P^k\sum_{l=0}^{k}(l+1)(l+2)a_{k-l}a_{l+2}\Big/\sum_{k=0}^{\infty}P^k\sum_{l=0}^{k}(l+1)(k-l+1)a_{l+1}a_{k-l+1}-1.$$

In particular, $\mu=2\frac{a_0a_2}{a_1^2}-1$ in the limit of vanishing pressure.

2. The Lennard-Jones potential can be written as $E_p(r)=E_0\left[\left(\frac{r_e}{r}\right)^{12}-2\left(\frac{r_e}{r}\right)^6\right]$, where E_0 is a positive constant and r_e is an equilibrium distance for which

$$E_p(r_e)=E_0\left[\left(\frac{r_e}{r}\right)^{12}-2\left(\frac{r_e}{r}\right)^6\right]_{r=r_e}=-E_0,$$

$$\frac{\mathrm{d}E_p}{\mathrm{d}r}(r_e)=-\frac{12E_0}{r_e}\left[\left(\frac{r_e}{r}\right)^{13}-\left(\frac{r_e}{r}\right)^7\right]_{r=r_e}=0,$$

$\frac{\mathrm{d}^2E_p}{\mathrm{d}r^2}(r_e)=\frac{12E_0}{r_e^2}\left[13\left(\frac{r_e}{r}\right)^{14}-7\left(\frac{r_e}{r}\right)^8\right]_{r=r_e}=\frac{72E_0}{r_e^2}>0$, which means that for $r=r_e$, $E_p(r)$ is minimal.

Assume that the volume of the system is proportional to the cube of the distance r, which translates into $V(r)=V_e\left(\frac{r}{r_e}\right)^3$, then:

$$E_p(r) = E_0\left[\left(\frac{V_e}{V}\right)^4 - 2\left(\frac{V_e}{V}\right)^2\right]$$ and

$$P(V) = -\frac{\partial E_p}{\partial V} = \frac{4E_0}{V_e}\left[\left(\frac{V_e}{V}\right)^5 - \left(\frac{V_e}{V}\right)^3\right]$$

One should note that $P(V_e) = 0$, which means that, with this model, the pressure to apply to the system at equilibrium is null.

$$\kappa(V) = -\frac{1}{V}\frac{\partial V}{\partial P} \Leftrightarrow \frac{1}{\kappa(V)} = -V\frac{\partial P}{\partial V} = \frac{4E_0}{V_e}\frac{V}{V_e}\left[5\left(\frac{V_e}{V}\right)^6 - 3\left(\frac{V_e}{V}\right)^4\right] = \frac{4E_0}{V_e}\left[5\left(\frac{V_e}{V}\right)^5 - 3\left(\frac{V_e}{V}\right)^3\right]$$

hence :

$$\mu(V) = \frac{\partial \frac{1}{\kappa}}{\partial P} = \frac{\frac{\partial \frac{1}{\kappa}}{\partial V}}{\frac{\partial P}{\partial V}} = \frac{-\frac{4E_0}{V_e^2}\left[5\cdot 5\left(\frac{V_e}{V}\right)^6 - 3\cdot 3\left(\frac{V_e}{V}\right)^4\right]}{-\frac{4E_0}{V_e^2}\left[5\left(\frac{V_e}{V}\right)^6 - 3\left(\frac{V_e}{V}\right)^4\right]} = \frac{\left[25\left(\frac{V_e}{V}\right)^2 - 9\right]}{\left[5\left(\frac{V_e}{V}\right)^2 - 3\right]}$$ and

$$\boxed{\mu(V = V_e) = \mu(P = 0) = \frac{25-9}{5-3} = 8}$$

In the domain $0 < V \leq V_e$, $\mu(V)$ is an increasing function of V with $5 < \mu(V) \leq 8$.