# 4. Equation of state

## 3. Vinet equation of state

### 3.1 What is 'Vinet equation of state'?

The equation of state (EOS) is a relation among pressure ($P$), temperature ($T$) and volume ($V$), which is frequently used in geophysics for obtaining essential physical parameters. With a given amount of matter, one variable can be obtained if the other two are known by equation of state. Vinet equation of state is one of the frequently used EOSs and proposed by Rose et al. (1983) and Vinet et al. (1983) as follows:

$$P = 3K_{T0}\left(\frac{V}{V_0}\right)^{-\frac{2}{3}}\left[1-\left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right]\exp\left\{\frac{3}{2}(K'_{T0}-1)\left[1-\left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right]\right\} \tag{4.1.12}$$

, where $K_{T0}$ is bulk modulus and $K'_{T0}$ is the derivative of $K_{T0}$ with respect to pressure.

### 3.2 Derivation of Vinet equation of state

To derive the Vinet equation of state, we start from describing the atomic binding energy. The atomic binding energy can be approximated by:

$$E(a) = E_0(1+a)\exp(-a) \tag{4.3.1}$$

$$a = (r - r_0)/l \tag{4.3.2}$$

Where $a$ is the reduction of the atomic spacing, $r_0$ and $r$ are the interatomic distances at zero and high $P$, $l$ is the scaling length.

Assuming that the Helmholtz free energy $F$ is proportional to the atomic binding energy, therefore $F$ has a formula similar to Eq. (4.3.1), $F(a) = F_0(1+a)\exp(-a)$ with Eq. (4.3.2) $a = (r - r_0)/l$,

$$F(r) = F_0\left(1+\frac{r-r_0}{l}\right)\exp\left(-\frac{r-r_0}{l}\right) \tag{4.3.3}$$

, where $F_0$ is constant.

Expressing Eq. (4.3.3) by volumes at zero and high $P$, $V_0$ and $V$, as:

$$F(V) = F_0\left(1+\frac{V^{1/3}-V_0^{1/3}}{l}\right)\exp\left(-\frac{V^{1/3}-V_0^{1/3}}{l}\right) \tag{4.3.4}$$

, where $V = r^3$, $V = r_0^3$.

From Eq. (4.1.1), $P$ is:

$$\begin{aligned}
P = -\frac{\partial F(V)}{\partial V} &= -F_0\left[\left(1+\frac{V^{1/3}-V_0^{1/3}}{l}\right)'\exp\left(-\frac{V^{1/3}-V_0^{1/3}}{l}\right)\right.\\
&\left.+\left(1+\frac{V^{1/3}-V_0^{1/3}}{l}\right)\left\{\exp\left(-\frac{V_0^{1/3}-V^{1/3}}{l}\right)\right\}'\right]\\
&= -F_0\left[\frac{1}{3l}V^{-\frac{2}{3}}\exp\left(-\frac{V^{1/3}-V_0^{1/3}}{l}\right)\right.\\
&\left.+\left(1+\frac{V^{1/3}-V_0^{1/3}}{l}\right)\left(-\frac{1}{3l}V^{-\frac{2}{3}}\right)\exp\left(\frac{V_0^{1/3}-V^{1/3}}{l}\right)\right]\\
&= -\frac{F_0}{3l^2}V^{-\frac{2}{3}}\left(V_0^{1/3}-V^{1/3}\right)\exp\left(\frac{V_0^{1/3}-V^{1/3}}{l}\right)
\end{aligned} \qquad (4.3.5)$$

We need to express Eq. (4.3.5) without using neither $F_0$ nor $l$ by using the macroscopic parameters, $K_{T0}$ and $K'_{T0}$. $K_{T0}$ is obtained firstly as:

$$\begin{aligned}
\left(\frac{\partial P}{\partial V}\right)_T &= \frac{\partial}{\partial V}\left[\frac{F_0}{3l^2}V^{-\frac{2}{3}}\left(V_0^{\frac{1}{3}}-V^{\frac{1}{3}}\right)\exp\left(\frac{V_0^{1/3}-V^{1/3}}{l}\right)\right]\\
&= \frac{F_0}{3l^2}\left[-\frac{2}{3}V^{-\frac{5}{3}}\left(V_0^{\frac{1}{3}}-V^{\frac{1}{3}}\right)+V^{-\frac{2}{3}}\left(-\frac{1}{3}V^{-\frac{2}{3}}\right)\right.\\
&\left.+V^{-\frac{2}{3}}\left(V_0^{\frac{1}{3}}-V^{\frac{1}{3}}\right)\left(-\frac{1}{3l}V^{-\frac{2}{3}}\right)\right]\exp\left(\frac{V_0^{1/3}-V^{1/3}}{l}\right)\\
&= \frac{F_0}{9l^3}\left[-2lV_0^{\frac{1}{3}}V^{-\frac{5}{3}}+\left(l-V_0^{\frac{1}{3}}\right)V^{-\frac{4}{3}}+V^{-1}\right]\exp\left[\left(V_0^{\frac{1}{3}}-V^{\frac{1}{3}}\right)/l\right]
\end{aligned} \qquad (4.3.6)$$

$$K_T = -V\left(\frac{\partial P}{\partial V}\right)_T = \frac{F_0}{9l^3}\left[2lV_0^{\frac{1}{3}}V^{-\frac{2}{3}}-\left(l-V_0^{\frac{1}{3}}\right)V^{-\frac{1}{3}}-1\right]\exp\left[\left(V_0^{\frac{1}{3}}-V^{\frac{1}{3}}\right)/l\right] \qquad (4.3.7)$$

By substituting $V$ by $V_0$,

$$K_{T0} = \frac{F_0}{9l^3}\left[2lV_0^{\frac{1}{3}}V_0^{-\frac{2}{3}}-\left(l-V_0^{\frac{1}{3}}\right)V_0^{-\frac{1}{3}}-1\right]\exp\left[\left(V_0^{\frac{1}{3}}-V_0^{\frac{1}{3}}\right)/l\right] = \frac{F_0}{9l^2}V_0^{-\frac{1}{3}} \qquad (4.3.8)$$

From Eq. (4.3.7), $K'_T$ and $K'_{T0}$ are obtained as:

$$K'_T = \left(\frac{\partial K_T}{\partial P}\right)_T = \left(\frac{\partial K_T}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial K_T}{\partial V}\right)_T\Big/\left(\frac{\partial P}{\partial V}\right)_T \qquad (4.3.9)$$

$$\begin{aligned}
\left(\frac{\partial K_T}{\partial V}\right)_T &= \frac{F_0}{27l^4}\left[V^{-\frac{2}{3}}+\left(l-V_0^{\frac{1}{3}}\right)V^{-1}+\left(l^2-3V_0^{\frac{1}{3}}l\right)V^{-\frac{4}{3}}\right.\\
&\left.-4V_0^{\frac{1}{3}}l^2V^{-\frac{5}{3}}\right]\exp\left[\left(V_0^{\frac{1}{3}}-V_0^{\frac{1}{3}}\right)/l\right]
\end{aligned} \qquad (4.3.10)$$

$$K'_T = \frac{1}{3l}\frac{V^{-\frac{2}{3}}+\left(l-V_0^{\frac{1}{3}}\right)V^{-1}+\left(l^2-3V_0^{\frac{1}{3}}l\right)V^{-\frac{4}{3}}-4V_0^{\frac{1}{3}}l^2V^{-\frac{5}{3}}}{-2lV_0^{\frac{1}{3}}V^{-\frac{5}{3}}+\left(l-V_0^{\frac{1}{3}}\right)V^{-\frac{4}{3}}+V^{-1}} \qquad (4.3.11)$$

By substituting Eq. (4.3.6) into Eq. (4.3.11):

$$K'_{T0} = \left(\frac{\partial K}{\partial V}\right)_{T,P=0} = \frac{1}{3l}\frac{V_0^{-\frac{2}{3}} + \left(l - V_0^{\frac{1}{3}}\right)V_0^{-1} + \left(l^2 - 3V_0^{\frac{1}{3}}l\right)V_0^{-\frac{4}{3}} - 4V_0^{\frac{1}{3}}l^2V_0^{-\frac{5}{3}}}{-2lV_0^{\frac{1}{3}}V_0^{-\frac{5}{3}} + \left(l - V_0^{\frac{1}{3}}\right)V_0^{-\frac{4}{3}} + V_0^{-1}} \tag{4.3.12}$$

$$= 1 + \frac{2}{3l}V_0^{\frac{1}{3}}$$

Before replacing $F_0$ and *l* by $K_{T0}$ and $K'_{T0}$, we need to transform Eq. (4.3.5) to:

$$\mathrm{P} = -3\frac{F_0}{9l^2V_0^{1/3}}(V/V_0)^{-\frac{2}{3}}\left(1 - (V/V_0)^{1/3}\right)\exp\left\{\frac{3}{2}\frac{2V_0^{1/3}}{3l}\left[1 - V_0^{1/3}\right]\right\} \tag{4.3.5}$$

Substituting Eq. (4.3.8) and Eq. (4.3.12) into Eq. (4.3.5), we get the Vinet's EOS:

$$P = 3K_{T0}\left(\frac{V}{V_0}\right)^{-\frac{2}{3}}\left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right]\exp\left\{\frac{3}{2}(K'_{T0} - 1)\left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right]\right\} \tag{4.1.12}$$