Complete Equations of State for PETN and Its Products from Atomistic Simulations — Supplementary Information

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On the equation of state for products

Common and convenient assumptions for equations of state are constant values for C_v and Γ, independent of density and temperature. If those assumptions were valid for PETN products, the MD data in figure 1 could be well approximated with linear fits. However, we can see in figure 1 that this is not the case.

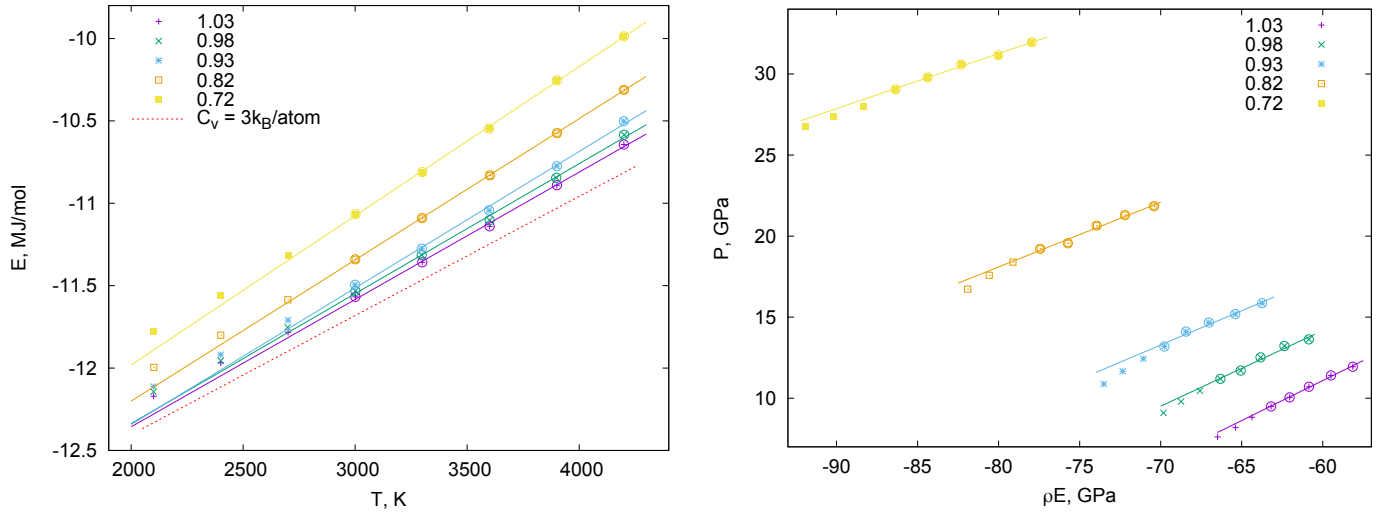

Figure 1: The explosive products equation of state based on molecular dynamics calculations. Left: internal energy as a function of temperature. The line corresponding to the heat capacity $3R$ per mole of atoms is shown for comparison. Right: pressure as a function of the internal energy density. The points corresponding to the conditions where equilibrium chemical composition was reached during simulation are encircled.

We used linear functions as the first approximation. The most reliable values were obtained for high temperatures, so $T_0 = 3600$ K was chosen as reference for the thermal decomposition products. The values of heat capacity C_v and Grüneisen parameter Γ at each V/V_0 were determined from the corresponding graphs as the angular coefficients of straight lines passing through the five points where equilibrium chemical composition was reached.

The functions $C_v = \phi(V)$ and $\Gamma = \gamma(V)$ of specific volume at T_0 are shown in figure 2.

The Grüneisen coefficient depends linearly on V:

$$\gamma(V) = \beta\frac{V}{V_0}, \ \beta = 0.474. \tag{1}$$

The parameters of the equations for products must comply with the compatibility conditions, as it is discussed in the main text. The function $\gamma(V)/V$ is non-increasing. The second condition leads to the following.

The results of molecular dynamics simulations (see fig. 1, 2) show that for the considered system $(\partial C_v/\partial V)_T$ and $(\partial\Gamma/\partial T)_V$ are negative, while $(\partial C_v/\partial T)_V$ is positive. As both Γ and C_v depend on temperature, the representation becomes indeterminate.

Let us seek for solutions in the form $C_v(V,T) = \phi(V)f(T)$, $\Gamma(V,T) = \gamma(V)g(T)$. Then the compatibility condition transforms to

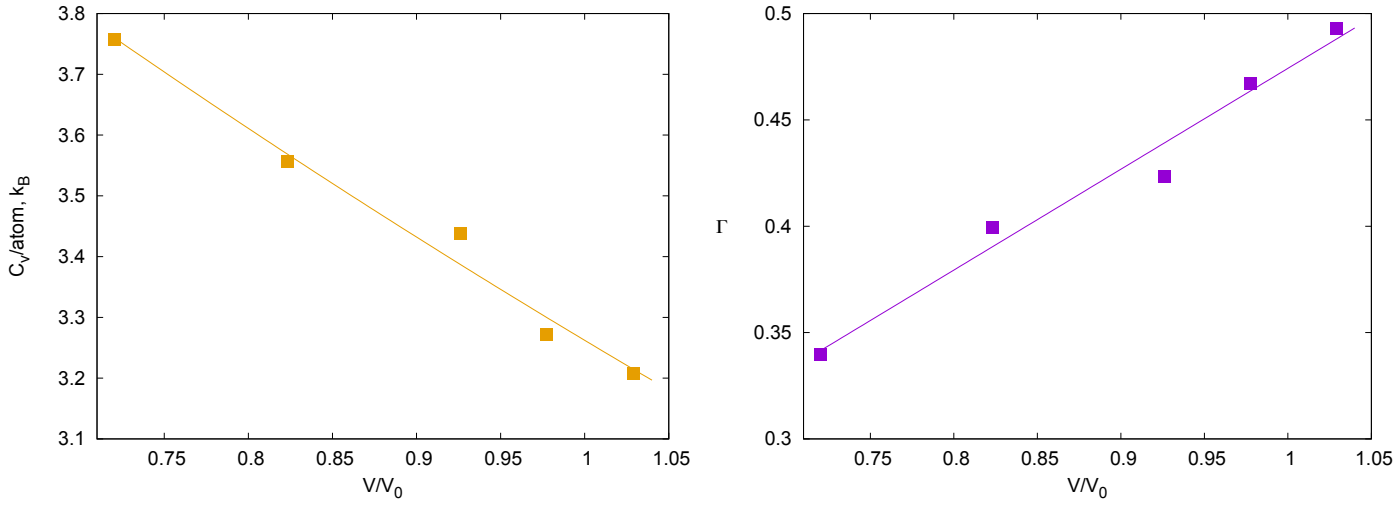

Figure 2: Left: heat capacity at constant volume as a function of V/V_0. Right: Grüneisen parameter as a function of V/V_0. Temperature $T_0 = 3600$ K.

$$V\frac{\mathrm{d}\phi(V)}{\mathrm{d}V}f(T) = T\gamma(V)\phi(V)\left(f(T)\frac{\mathrm{d}g(T)}{\mathrm{d}T} + g(T)\frac{\mathrm{d}f(T)}{\mathrm{d}T}\right). \tag{2}$$

Partial derivatives were replaced with full ones due to separation of variables. We combine all factors not depending on temperature in the left part of the equation. As heat capacity at finite temperatures is never zero, both parts may be divided by $f(T)$:

$$\frac{V}{\gamma(V)\phi(V)}\frac{\mathrm{d}\phi(V)}{\mathrm{d}V} = \alpha(V,T) = T\left(\frac{\mathrm{d}g(T)}{\mathrm{d}T} + g(T)\frac{\mathrm{d}\ln f(T)}{\mathrm{d}T}\right). \tag{3}$$

The left part of the equation (3) is a unitless function of only V, the right one is a unitless function of only T. For the equation (3) to be satisfied at various V and T (i.e. for the variables for Γ and C_v to be actually separated), one must state $\alpha(V,T) \equiv \alpha \in \mathbb{R}$.

This condition gives the function $Cv(V)$. Substituting $\gamma(V)$ from equation (1), we have

$$\frac{V_0}{\beta\phi(V)}\frac{\mathrm{d}\phi(V)}{\mathrm{d}V} = \alpha, \tag{4}$$

$$\phi(V) = C_0 \exp\left(\alpha\beta\frac{V}{V_0}\right). \tag{5}$$

The fit to MD data gives $C_0 = 5.42k_B$, $\alpha = -1.07$. The corresponding approximation is shown in the left part of fig. 2.

The obtained functions of volume describe simulation data well, but they have undesirable asymptotics at large V. The parameter Γ fast and infinitely grows with lowering density. This in turn leads to C_v rapidly approaching zero. We extrapolate the dependency $\gamma(V)$ in the region $V > V_0$ at T_0 so that $\lim_{V\to\infty}\gamma(V) = \gamma_\infty = \frac{2}{3}$. This corresponds to the Grüneisen parameter of ideal gas. Imposing the continuity of $\gamma(V)$ and $\mathrm{d}\gamma(V)/\mathrm{d}(V/V_0)$ at $V = V_0$, we obtain

$$\gamma(V > V_0) = \gamma_\infty + (\beta - \gamma_\infty)\left(\frac{V}{V_0}\right)^{\frac{\beta}{\beta-\gamma_\infty}} = \frac{2}{3} - 0.18\left(\frac{V}{V_0}\right)^{-2.77}. \tag{6}$$

Then the form of $\phi(V)$ in this range of V is again defined by the left part of the equation (3):

$$\begin{aligned}\phi(V > V_0) &= \phi(V_0)\left(\frac{V}{V_0}\right)^{\alpha\gamma_\infty}\exp\left(\frac{\alpha(\beta-\gamma_\infty)^2}{\beta}\left[\left(\frac{V}{V_0}\right)^{\frac{\beta}{\beta-\gamma_\infty}} - 1\right]\right) = \\ &= 3.2k_B\left(\frac{V}{V_0}\right)^{-0.71}\exp\left(-0.068\left[\left(\frac{V}{V_0}\right)^{-2.77} - 1\right]\right).\end{aligned} \tag{7}$$

The function $\phi(V)$ and its first derivative are also continuous at V_0. The graphs for $\phi(V)$ and $\gamma(V)$ in wide range of densities are shown in figure 3.

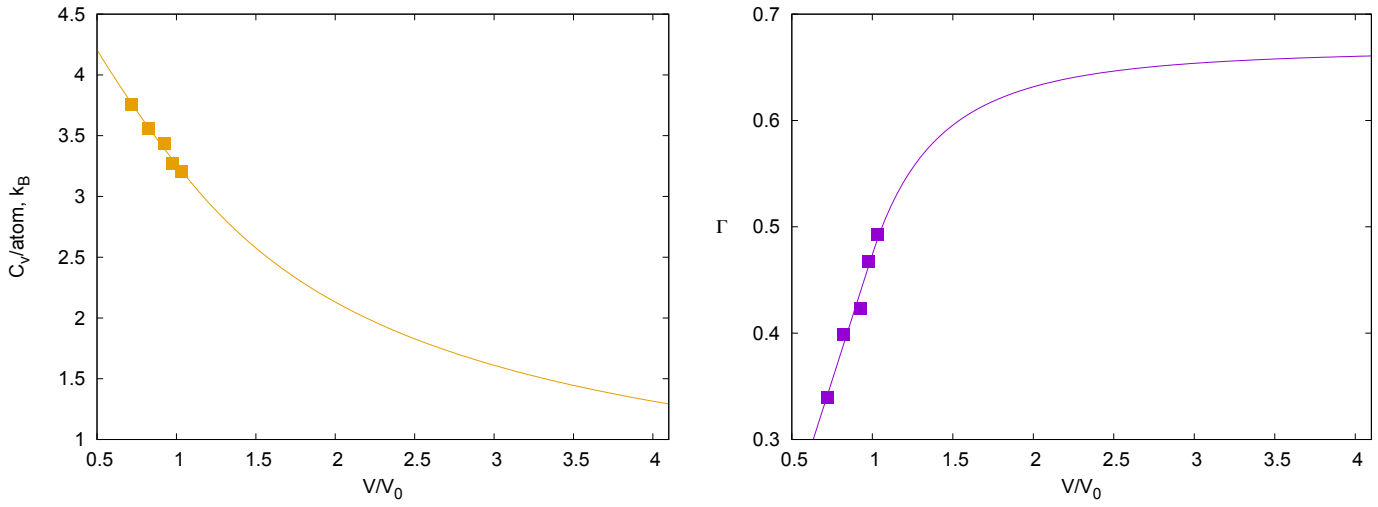

Figure 3: The proposed extrapolation of the dependencies of C_v (left) and Γ (right) on V/V_0 at $T_0 = 3600$ K to the low density region. Points show the molecular dynamics data.

Similarly to the dependencies on V, the right side of the equation (3) includes two functions $f(T)$ and $g(T)$, so that not one of them is determined and there is only the relation between the two. To solve the equation it is necessary to state the form of one of the functions *a priori*. The suitable form should give the expressions for f and g in elementary functions for the equation of state to remain not very demanding computationally.

We state exactly

$$g(T) = 1 + \lambda\alpha \ln \frac{T}{T_0}, \ \lambda \in \mathbb{R}. \tag{8}$$

Then the equation with separable variables is obtained for $C_v(T)$:

$$\frac{\mathrm{d} \ln f(T)}{\mathrm{d}T} = \frac{(1-\lambda)\alpha}{T\left(1 + \lambda\alpha \ln \frac{T}{T_0}\right)}, \tag{9}$$

the solution of which with the boundary condition $f(T_0) = 1$ is

$$f(T) = \left[1 + \lambda\alpha \ln \frac{T}{T_0}\right]^{\frac{1-\lambda}{\lambda}} = [g(T)]^{\frac{1-\lambda}{\lambda}}. \tag{10}$$

The parameter λ characterizes the degree of deviation of $E(T)$ and $P(\rho E)$ from linearity (fig. 1) and must be fitted to reproduce simulation results. To determine λ we expand the temperature dependencies of C_v and Γ to the first order in $\Delta T = T - T_0$ and $\Delta[\rho E] = [\rho E] - [\rho E]_0$ near T_0, $[\rho E]_0$:

$$f(\Delta T) \approx 1 + (1-\lambda)\alpha \frac{\Delta T}{T_0}, \tag{11}$$

$$g(\Delta[\rho E]) \approx 1 + \lambda\alpha \frac{\Delta T}{T_0} \approx 1 + \lambda\alpha \frac{\Delta[\rho E]}{\rho C_v(V) T_0}. \tag{12}$$

In the equation (12) while expressing ΔT through the energy density the dependence of C_v on temperature is not taken into account as it contributes to the next order in the expansion. In this approximation the simulation data is fitted with parabolas:

$$\begin{aligned} E(T) &= E(T_0) + \phi(V) \int_0^{T-T_0} f(\Delta T)\, \mathrm{d}(\Delta T) \approx \\ &\approx E(T_0) + \phi(V)(T - T_0)\left[1 + \frac{(1-\lambda)\alpha}{2} \frac{T - T_0}{T_0}\right], \end{aligned} \tag{13}$$

$$P([\rho E]) = P([\rho E]_0) + \gamma(V) \int_0^{[\rho E]-[\rho E]_0} g(\Delta[\rho E])\, \mathrm{d}(\Delta[\rho E]) \approx$$
$$\approx P([\rho E]_0) + \gamma(V)([\rho E] - [\rho E]_0) \left[1 + \frac{\lambda\alpha}{2} \frac{[\rho E] - [\rho E]_0}{\rho\phi(V)T_0}\right]. \tag{14}$$

The non-linear fit gives $\lambda = 1.51$, the consistency between the obtained equation of state and the molecular dynamics data is presented in figure 4.

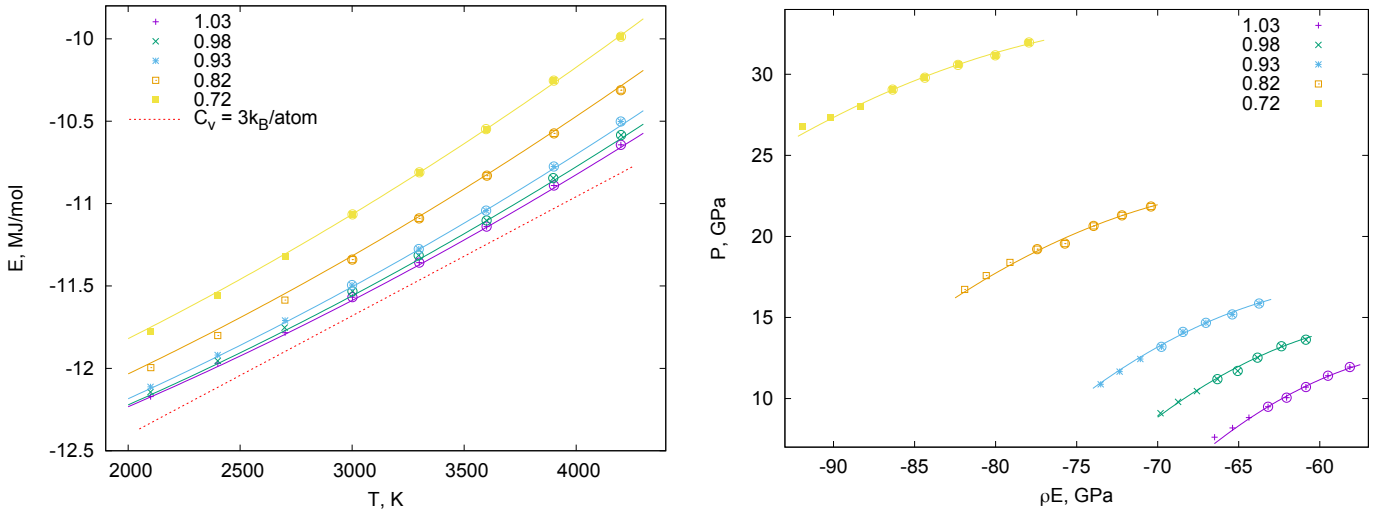

Figure 4: Approximation of the molecular dynamics data with C_v and Γ depending on volume and temperature.

The general form of $f(T)$ and $g(T)$ in a wide range of temperatures, as well as their approximation in accordance with the equations (11) and (12), are shown in figure 5.

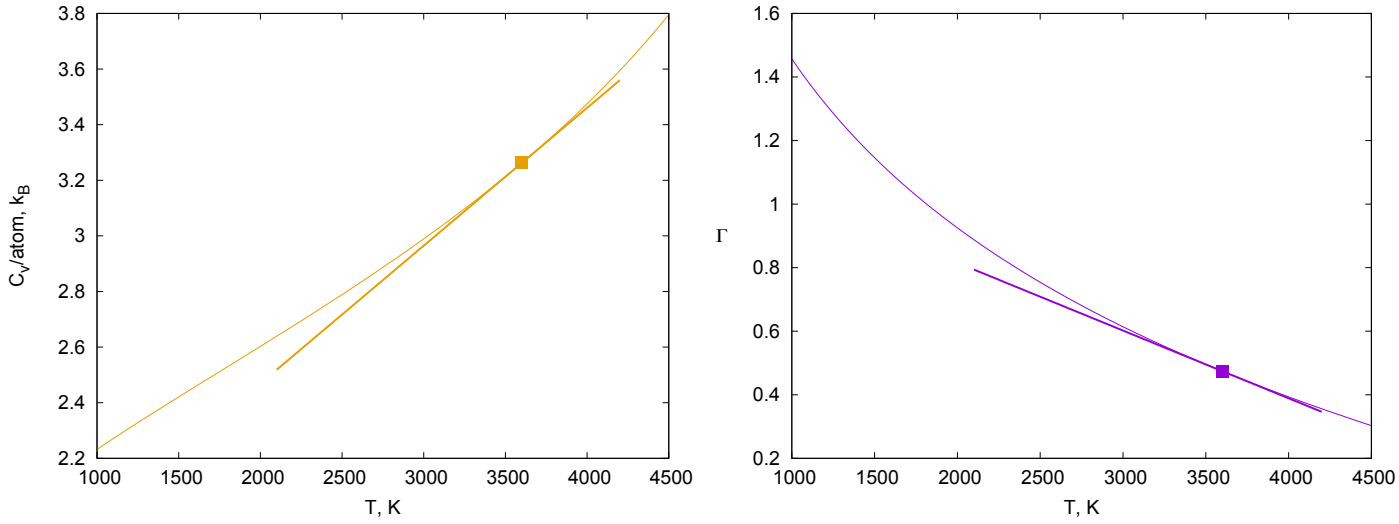

Figure 5: Temperature dependencies of C_v (left) and Γ (right) from 1000 to 4500 K at $V = V_0$. The $T_0 = 3600$ K is denoted with points, linear segments demonstrate the temperature range and approximations used to determine the value of λ.

Finally, combining all together, we obtain the following expressions for C_v and Γ:

$$C_v(V,T) = \phi(V)\left(1+\lambda\alpha\ln\frac{T}{T_0}\right)^{\frac{1-\lambda}{\lambda}}, \tag{15}$$

$$\phi(V) = \begin{cases} C_0\exp\left(\alpha\beta\frac{V}{V_0}\right), \ V \le V_0, \\ C_0\exp(\alpha\beta)\left(\frac{V}{V_0}\right)^{\alpha\gamma_\infty}\exp\left(\frac{\alpha(\beta-\gamma_\infty)^2}{\beta}\left[\left(\frac{V}{V_0}\right)^{\frac{\beta}{\beta-\gamma_\infty}}-1\right]\right), \ V > V_0, \end{cases} \tag{16}$$

$$\Gamma(V,T) = \gamma(V)\left(1+\lambda\alpha\ln\frac{T}{T_0}\right), \tag{17}$$

$$\gamma(V) = \begin{cases} \beta\frac{V}{V_0}, \ V \le V_0, \\ \gamma_\infty + (\beta-\gamma_\infty)\left(\frac{V}{V_0}\right)^{\frac{\beta}{\beta-\gamma_\infty}}, \ V > V_0, \end{cases} \tag{18}$$

where $T_0 = 3600$ K, $V_0 = 0.56$ cm^3/g, the parameters fitted to MD data are $\alpha = -1.07$, $\beta = 0.474$, $\lambda = 1.51$, $C_0 = 5.42k_B$, and γ at T_0 and infinite volume is $\gamma_\infty = 2/3$.