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Sublimation rate of molecular crystals – role of internal degrees of freedom

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Abstract:

It is a common practice to estimate site desorption rate from crystal surfaces with an Arrhenius expression of the form $v_{eff} \exp(-\Delta E/k_B T)$, where ΔE is an activation barrier to desorb and v_{eff} is an effective vibrational frequency $\sim 10^{12} \text{ sec}^{-1}$. However, such a formula can lead to *several to many orders of magnitude* underestimation of sublimation rates in molecular crystals due to internal degrees of freedom. We carry out a quantitative comparison of two energetic molecular crystals with crystals of smaller entities like ice and Argon (solid) and uncover the errors involved as a function of molecule size. In the process, we also develop a formal definition of v_{eff} and an accurate working expression for equilibrium vapor pressure.

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Kinetics of atoms and molecules at surfaces involving adsorption, desorption and diffusion is an important phenomenon that govern many physical processes. These include sublimation, evaporation and condensation, growth and long-term stability of crystals and thin-films, crystal morphology evolution, action of chemical/molecular sensors, rate of establishing solid-vapor and liquid-vapor equilibrium, among others. Such processes are directly relevant to diverse disciplines including materials science, chemical engineering, molecular biology and medicine, meteorology, geochemistry, and planetary science. Equilibrium between the condensed phase (solid, liquid) and the gas phase (vapor) is established when the rate of sublimation/evaporation from the condensed phase surface is equal to the rate of condensation from the vapor phase. Computing either of these quantities accurately is challenging. While the rate of influx of vapor-phase atoms/molecules onto the condensed surface is given simply by the Knudsen's formula [1, 2] $p / \sqrt{2\pi mk_B T}$, where p is the vapor pressure and m the mass of the atomic/molecular species, the probability of incorporation into the surface, known as the sticking coefficient depends on the atomic details of the surface, as well as the energy, orientation and impingement direction of the incoming particle. Similarly, desorption rate from individual sites depend on the local environment (coordination) of the site, and can involve either direct evaporation into the vapor phase or a multistep process involving surface migration to different sites followed finally by detachment.

With specific interest in the rate of mass loss of energetic materials through sublimation, we attempted to estimate the desorption rate of such molecules from various crystal faces. Assuming that all desorption processes effectively start from "kink" sites [1] on any exposed face, one can estimate a net evaporation rate by the equation [3]:

$$\dot{\phi}_{simple}^{\uparrow} = \theta v_{eff} \exp(-\Delta E / k_B T), \quad (1)$$

where θ is the surface density of kink sites, v_{eff} is an effective vibrational frequency, and ΔE the desorption energy from the kink site, which is related to the heat of sublimation ΔH by the equation $\Delta E = \Delta H - pV = \Delta H - k_B T$ (since the ideal gas law is applicable for such typical low-vapor-pressure systems). The physical reasoning behind Eq. (1) is that the molecular/atomic species vibrates with a frequency v_{eff} and during each of those oscillations it has a probability $\exp(-\Delta E/k_B T)$ to desorb from the surface. However, for most

molecular crystals Eq. (1) severely underestimates the rate of sublimation. Thus, for concreteness, let us consider two energetic materials, i.e., Pentaerythritol Tetranitrate (PETN) and the β -polymorph of Tetrahexamine Tetranitramine (β -HMX), which consist of 29 and 28 atoms, respectively (Fig. 1). PETN in its common form (PETN-I) crystallizes in a body-centered tetragonal structure [4] with a heat of sublimation of ΔH of ~ 35.1 kcal/mol [5], while β -HMX crystallizes in a monoclinic structure [6] with a heat of sublimation of ~ 44.2 kcal/mol [7]. Assuming a $v_{eff} \sim 10^{12}$ sec⁻¹ and a maximum kink density of $\theta = 1$, Eq. (1) yields sublimation rates lower by 8-10 orders of magnitude as compared to experimentally measured value for either PETN [5] or HMX [8]. The above problem of sublimation rate could be equivalently stated in terms of equilibrium vapor pressure. Thus, equating the incoming flux (given by Knudsen's formula) with the outgoing flux estimated by Eq. (1), one obtains the following formula for the equilibrium vapor pressure p :

$$p_{simple} = \frac{e\theta v_{eff}}{\alpha\kappa} \sqrt{2\pi mk_B T} \exp(-\Delta H / k_B T), \quad (2)$$

where κ is an average sticking coefficient and α the area per surface site. As will be shown below, the above formula (assuming κ and θ of the order of unity) underestimates the equilibrium pressure of PETN and HMX by 10 orders of magnitude as compared to experiments.

As a remedy to the large discrepancies mentioned above, one needs to replace Eq. (1) with one derived from the reaction rate theory [3, 9], which has previously been used to compute the sublimation rate of molecular crystals [10]. However, the rate of mass loss (i.e. sublimation) depends significantly on the details of the experimental conditions (e.g., the presence of a carrier gas, boundary layer, etc.), particle morphology (i.e., fraction of different exposed facets), surface roughness, and so on. So, we focus instead on deriving an accurate formula for the equilibrium vapor pressure p , a data that is widely available for many crystals as a function of temperature. To this end, we use the harmonic approximation to express the chemical potential of the solid and the vapor phase as [11]:

$$\mu_s = \varepsilon_s - k_B T \int dv g_{ph}(v) \ln \{Z_{vib}(v)\}, \quad (3)$$

and

$$\mu_v = \varepsilon_v + 3k_B T \ln(\Lambda) - k_B T \ln(k_B T / p) - k_B T \ln(Z_{rot}) - k_B T \sum_{j=1}^{3N_M-6} \ln\{Z_{vib}(v_j)\} . \quad (4)$$

In Eq. (3) and (4) subscripts “s” and “v” denote solid and vapor phase, ε_s , ε_v are the reference potential energies of the two phases, N_M the number of atoms in a molecule, $g_{ph}(v)$ the phonon density of states (DOS) for the solid with a normalization of $\int dv g_{ph}(v) = 3N_M$, $\Lambda = h / \sqrt{2\pi mk_B T}$ the thermal (or de Broglie) wavelength, and the vibrational and rotational partition functions are given by:

$$Z_{vib}(v) = \frac{\exp(-hv / 2k_B T)}{1 - \exp(-hv / k_B T)} \quad (5)$$

$$\text{and } Z_{rot} = \frac{\pi^{1/2} (8\pi^2 k_B T)^{3/2} (I_1 I_2 I_3)^{1/2}}{\sigma h^3} , \quad (6)$$

where I_1 , I_2 , and I_3 are the principal moments of inertia, and σ is a symmetry factor given by the number of proper rotational symmetry operations for an isolated molecule [11, 12]. At thermodynamic equilibrium the chemical potentials μ_s and μ_v must be equal, leading to the following expression for p :

$$p = Z_{rot} \frac{k_B T}{\Lambda^3 \{Z_{vib}(v_{eff})\}^6} \exp\{-(\varepsilon_v - \varepsilon_s) / k_B T\} , \quad (7)$$

where we have defined an effective frequency v_{eff} through the equation:

$$\begin{aligned} 6 \ln\{Z_{vib}(v_{eff})\} &= \left[\int dv g_{ph}(v) \ln\{Z_{vib}(v)\} - \sum_{j=1}^{3N_M-6} \ln\{Z_{vib}(v_j)\} \right] , \\ &= \ln\{Z_{vib}(solid) / Z_{vib}(vapor)\} \end{aligned} \quad (8)$$

Eq. (8) allows Eq. (7) to be written in the form:

$$p = \frac{k_B T}{\Lambda^3} \frac{Z_{rot} Z_{vib}(vapor)}{Z_{vib}(solid)} \exp\{-(\varepsilon_v - \varepsilon_s) / k_B T\} , \quad (9)$$

a form closely related to site-desorption rates derived from reaction rate theory [3, 9]. For practicality of computation, however, we re-write Eq. (7) as:

$$p = p_0 \exp(-\Delta H / k_B T), \quad (10)$$

where the prefactor is given by:

$$p_0 = Z_{rot} \frac{k_B T}{\Lambda^3 \{Z_{vib}(v_{eff})\}^6} \exp[\{\Delta H - (\varepsilon_v - \varepsilon_s)\} / k_B T]. \quad (11)$$

The quantity in the exponent of Eq. (11) can be evaluated using the Claius-Clapeyron equation

$\frac{\partial \ln p}{\partial \ln(1/k_B T)} = -\Delta H$, which yields:

$$\begin{aligned} \Delta H - (\varepsilon_v - \varepsilon_s) &= 4k_B T - \left\{ \int g_{ph}(v) dv \cdot f_{vib}(v) - \sum_{j=1}^{3N_M-6} f_{vib}(v_j) \right\}, \\ &= 4k_B T - 6f_{vib}(v_E) \left(1 - \frac{\partial \ln v_{eff}}{\partial \ln T} \right), \end{aligned} \quad (12)$$

where, $f_{vib}(v) = \frac{hv}{2} + \frac{hv}{\exp(hv/k_B T) - 1}$ is the vibrational free energy associated with a mode of frequency v , including the zero-point contribution.

With the availability of accurate class II force fields, especially for systems with organic functional groups, we attempted to compute the effective frequency v_{eff} through Eq. (8). To this end, both the phonon DOS $g_{ph}(v)$ and the $(3N_M-6)$ molecular vibration frequencies v_j of PETN were computed using the Accelrys module IR/Raman [13] and three different force fields: Universal (UFF) [14], CVFF [15], and COMPASS [16]. Although the individual mode frequencies computed by the force fields are in good agreement with each other (within 3-4 %), the computed values of v_{eff} for PETN using the three force fields are quite different, being 7.15×10^{12} , 2.25×10^{13} , and $3.44 \times 10^{12} \text{ sec}^{-1}$ for UFF, CVFF, and COMPASS respectively. This large variation of v_{eff} stems from the difficulty in accurately modeling the phonon-vibron coupling, which is usually not a criterion on which development of force fields are based. Assuming that the true v_{eff}

lies somewhere within the range of the three computed values, a value of $v_{eff} \sim 10^{13} \text{ sec}^{-1}$ seems to be a reasonable choice for PETN. In addition, we also find that the variation of v_{eff} with T , i.e., $\partial \ln v_{eff} / \partial \ln T$ is small, with an absolute value < 0.1 for all three force fields. Considering our aim of accuracy to within an order of magnitude, this term could therefore be safely dropped from Eq. (12).

Table 1 displays the computed values of equilibrium pressure using both the simple equation (2) and the more accurate equations (10)-(12) and compare with experimental values for the temperature range of 300-400K [5]. Several results are worth noting: (i) pressure computed with Eq. (10)-(12) is in excellent agreement with experiment over the entire 100 K temperature range; (ii) pressure computed by the simple formula (Eq. (2)) is underestimated by 10 orders of magnitude over the entire temperature range; and (iii) the product of Z_{rot} and $\{Z_{vib}(v_{eff})\}^{-6}$ (see Eq. (11)) account for almost 8 orders of magnitude of this discrepancy.

To illustrate that the previous results are true not just for PETN as a special case, but rather generic for molecules of such size, we list in table 2 similar results for β -HMX. Here we chose v_{eff} so as to yield the best fit of computed p to the experimental values over the entire temperature range. A comparison between tables 1 and 2 makes it clear that the results are not only qualitatively but also quantitatively similar. Given that p_{simple} underestimates vapor pressure by 10 orders of magnitude in either case, the question arises as to whether Eqs. (1) and (2) are at all applicable in any situation. To address this point, we compare in Table 3 results for PETN and β -HMX with a smaller molecule, i.e., water frozen in the ice-I_h structure [17], and an atomic system, i.e., Argon (Ar) crystallized in a cubic close-packed structure [18]. We chose a specific temperature for each system, i.e., room temperature (300 K) for PETN, the lower limit of published data (350 K) for HMX [7], the melting point of ice (273 K), and the melting point of Ar (84 K) under ambient conditions. Two observations are evident. First, the smaller the molecule, the smaller the v_{eff} . Thus, as compared to PETN, v_{eff} is reduced by roughly 36% for ice, and 89% for Ar. Second, relative to PETN and HMX, p_{simple} yields a much better vapor pressure for ice, although it is still underestimated by 3 orders of magnitude. For Ar, on the other hand, p_{simple} gets the pressure correct to within a factor of 2. The result correlates well with the product of Z_{rot} and $\{Z_{vib}(v_{eff})\}^{-6}$, which are much smaller than for PETN or HMX.

In summary, we find that for non-covalently bonded solids the simple and oft-used Eq. (1) is a reasonable approximation only when the molecular entities are very small, consisting of one or just a few atoms (i.e. possess only a few degrees of freedom). For larger molecules both Z_{rot} and $\{Z_{vib}(v_{eff})\}^{-6}$, especially the former can become large leading to the failure of Eq. (1) and (2) by many orders of magnitude. Physically, the large value of Z_{rot} can be interpreted as a large number of independent rotational states or channels the molecule from the surface can desorb into. The effect is magnified when dealing with the adsorption and desorption of biomolecules like antigens and proteins. In the course of this exercise, we have derived an appropriate definition of the effective vibrational frequency v_{eff} , and an accurate working expression for the equilibrium pressure p . Recognition of the limitations of Eq. (1) (and Eq. (2)) has important ramifications for many application areas, including surface density of adsorbates (Langmuir isotherms) [22], residency times of analytes on sensor surfaces [23, 24], interpretation of binding energy from thermal desorption spectroscopy (TDS) data, molecular (antigen, drug) binding efficiency at intra- and extra-cellular receptor sites, and so on.

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Table 1. Computed and experimental vapor pressure for PETN. Relevant parameters: $m=316.2$ a.u., $N_M = 29$, $\nu_{\text{eff}} = 1.0 \times 10^{13} \text{ sec}^{-1}$, $\Delta H = 35.1 \text{ kcal/mol}$. For p_{simple} we assume $\kappa, \theta = 1$, and use an average (face-independent) $\alpha = \nu_s^{2/3}$, where $\nu_s =$ volume per molecule in the crystal. Experimental data from ref. [5].

T (K)	$\{Z_{\text{vib}}(\nu_{\text{eff}})\}^{-6}$	Z_{rot}	$p_{\text{simple}} \text{ (erg/cm}^3\text{)}$ (Eq. (2))	$p \text{ (erg/cm}^3\text{)}$ (Eq. (10)-(12))	$p \text{ (erg/cm}^3\text{)}$ (experimental)
300	31.47	4.64×10^6	1.90×10^{-15}	3.48×10^{-5}	2.99×10^{-5}
325	17.77	5.23×10^6	1.83×10^{-13}	2.99×10^{-3}	2.78×10^{-3}
350	10.59	5.85×10^6	9.24×10^{-12}	1.34×10^{-1}	1.35×10^{-1}
375	6.60	6.48×10^6	2.77×10^{-10}	3.58×10^0	3.91×10^0
400	4.27	7.14×10^6	5.43×10^{-9}	6.25×10^1	7.42×10^1

Table 2. Table 1 re-computed for β -HMX. Relevant parameters are: $m=296.2$ a.u., $N_M = 28, v_{eff} = 9.2 \times 10^{12}$ sec^{-1} , and $\Delta H = 44.2$ kcal/mol. Experimental data from ref. [7].

T (K)	$\{Z_{\text{vib}}(v_{\text{eff}})\}^{-6}$	Z_{rot}	p_{simple} (erg/cm ³) (Eq. (2))	p (erg/cm ³) (Eq. (9)-(11))	p (erg/cm ³) (experimental)
350	5.99	5.56×10^6	1.97×10^{-17}	1.65×10^{-7}	1.39×10^{-7}
375	3.76	6.17×10^6	1.40×10^{-15}	1.04×10^{-5}	0.96×10^{-5}
400	2.45	6.80×10^6	5.89×10^{-14}	3.85×10^{-4}	3.90×10^{-4}
425	1.65	7.44×10^6	1.60×10^{-12}	9.27×10^{-2}	1.03×10^{-2}
450	1.14	8.11×10^6	3.00×10^{-11}	1.55×10^{-1}	1.87×10^{-1}

Table 3. Comparison of computed and experimental vapor pressure for different systems: β -HMX, PETN, ice (I_h), and Argon (cubic close-packed). Each system is chosen at a different temperature to accommodate different phase stabilities and the availability of vapor pressure data. For computing p_{simple} , we assumed $\theta, \kappa = 1$ [19].

System \rightarrow	β -HMX	PETN	Ice (I_h)	Argon
T (K)	350	300	273	84
M (a.u.)	244	316	18	39.9
N_M	28	29	3	1
α (\AA^2)*	40.7	44.3	10.2	11.0
ΔH (kcal/mol)	44.2 [ref. 7]	35.1 [ref. 5]	12.2 [ref. 20]	1.6 [ref. 21]
v_{eff} (sec^{-1})	1.0×10^{13}	9.2×10^{12}	6.4×10^{12}	1.1×10^{12}
$\{Z_{vib}(v_{eff})\}^{-6}$	10.59	31.47	2.78	0.07
Z_{rot}	5.56×10^6	4.64×10^6	7.26×10^1	1.0
p_{simple} (erg/cm^3) (Eq. (2))	1.97×10^{-17}	1.90×10^{-15}	7.46×10^0	4.06×10^5
p (erg/cm^3) (Eq. (9)-(11))	1.65×10^{-7}	3.48×10^{-5}	5.91×10^3	8.33×10^5
p (erg/cm^3) (experimental)	1.39×10^{-7} [ref. 7]	2.99×10^{-5} [ref. 5]	6.03×10^3 [ref. 20]	7.16×10^5 [ref. 21]

*Estimated by $v_s^{2/3}$, where v_s is volume per molecule in the crystal phase

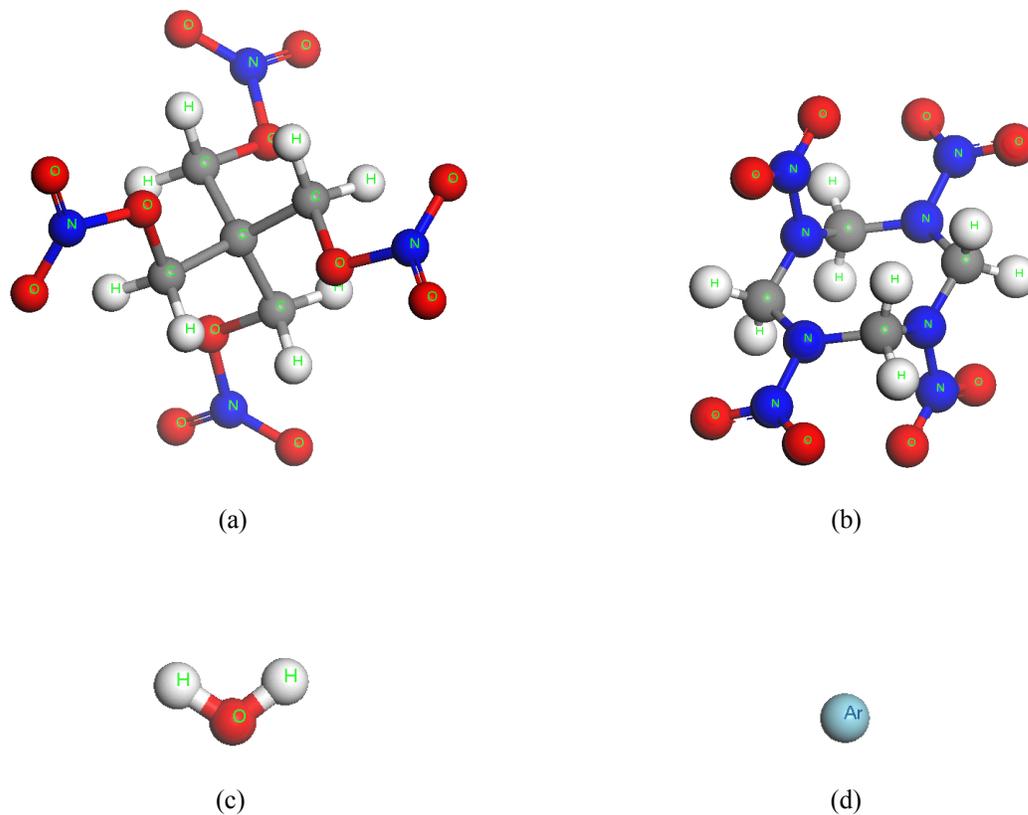


Fig. 1. Molecular models of: (a) PETN ($C_5H_8N_4O_{12}$, $N_M = 29$); (b) β -HMX ($C_4H_8N_8O_8$, $N_M = 28$); (c) water (H_2O , $N_M = 3$); (d) Argon (Ar, $N_M = 1$). Color scheme (online only): C (grey), H (white), N (blue), O (red).