Pebble rod recession kinetics under high heat loads

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1 Free pebble power balance

A rod made of carbon pebbles is heated by the CW laser under a vacuum atmosphere. The surface temperature of the rod rises and some of the pebbles are released from the surface at $T \approx 2000\,\mathrm{K}$.

The free pebble cools down through radiation and partially due to sublimation. Heat exchange with the atmosphere is neglected because the pressure in the chamber is $\approx 10^{-4}\,\mathrm{Torr}$. In the absence of any other power losses, the power balance requires:

$$\frac{dE}{dt} = \sigma\varepsilon A T^4(t) + P_{\mathrm{sub}}, \tag{1}$$

where P_{sub} is the heat loss due to sublimation, and the term $\sigma\varepsilon A T^4(t)$ corresponds to the radiative loss. The energy loss during the sublimation process is given by

$$E_{\mathrm{sub}} = H_{\mathrm{s}} n_{\mathrm{sub}}. \tag{2}$$

Here, H_{s} is the heat of sublimation in J/mol and n_{s} is the amount of substance sublimated, given in moles.

The rate (in atoms/s) of sublimation can be approximated by the Arrhenius relationship

$$r = r_0 \exp\left(-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}} T}\right), \tag{3}$$

where with E_{a} an activation energy for the sublimation process which is related to H_{s} and $k_B = 8.617 \times 10^{-5}\,\mathrm{eV/K}$ being the Boltzmann constant.

The power loss due to sublimation might be derived from Eqn. (2), by taking the time derivative:

$$P_{\mathrm{sub}} = \frac{dE_{\mathrm{sub}}}{dt} = H_{\mathrm{s}} \frac{dn_{\mathrm{sub}}}{dt} = H_{\mathrm{s}} \frac{1}{N_{\mathrm{A}}} \frac{dN_{\mathrm{sub}}}{dt}$$

with $N_{\mathrm{A}} = 6.022 \times 10^{23}\,\mathrm{mol}^{-1}$ the Avogadro constant. But dN/dt is just the sublimation rate r so,

$$P_{\mathrm{sub}} = H_{\mathrm{s}} \frac{r_0}{N_{\mathrm{A}}} \exp\left(-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}} T}\right). \tag{4}$$

Plugging Eqn. (4) into (1):

$$\frac{dE}{dt} = \sigma\varepsilon A T^4(t) + H_{\mathrm{s}} \frac{r_0}{N_{\mathrm{A}}} \exp\left(-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}} T}\right). \tag{5}$$

The energy of the system should be

$$E = c_{\mathrm{p}} \rho V_{\mathrm{hot}} \left(T_0 - T(t)\right). \tag{6}$$

Here, we differentiate V_{hot} from the total volume of the pebble because the T might not be uniform inside the pebble. Instead, to a good approximation, the temperature is uniform within the outer half shell of the pebble exposed to the laser beam, defined by the heat diffusion length:

$$V_{\mathrm{hot}} = \frac{2}{3}\pi \left[r^3 - (r - L_{\mathrm{d}})^3\right], \tag{7}$$

where $L_\mathrm{d} = \sqrt{\alpha t_{ex}}$ the thermal diffusion length of the pebble material and α the thermal diffusivity of the material and t_ex is the time the pebble has been exposed to the laser beam.

Using the chain rule on Eqn. (6):

$$\frac{dE}{dt} = \frac{dE}{dT}\frac{dT}{dt} = -c_\mathrm{p}\rho V_\mathrm{hot}\frac{dT}{dt} = \sigma\varepsilon A T^4(t) + H_\mathrm{s}\frac{r_0}{N_\mathrm{A}}\exp\left(-\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right) \tag{8}$$

The form of $T(t)$ is then obtained by integrating

$$-c_\mathrm{p}\rho V_\mathrm{hot}\frac{dT}{dt} = \sigma\varepsilon A T^4(t) + H_\mathrm{s}\frac{r_0}{N_\mathrm{A}}\exp\left(-\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right) \tag{9}$$

with respect to dt.

We assume that E_a is approximately $H_\mathrm{s} = (170.39 \pm 0.20)\,\mathrm{kcal/mol} = (7.39 \pm 0.01)\,\mathrm{eV}$ (Brewer *et al.* [1]).

Eqn. (7) can be written in terms of the sphere diameter:

$$V_\mathrm{hot} = \frac{2}{3}\pi\left[\frac{d^3}{8} - \left(\frac{d}{2} - L_\mathrm{d}\right)^3\right].$$

This equation can be reorganized as follows:

$$V_\mathrm{hot} = \frac{1}{12}\pi\left[d^3 - (d - 2L_\mathrm{d})^3\right].$$

The error in the diffusion length is given by

$$\delta L_\mathrm{d} = \frac{L_\mathrm{d}}{2}\sqrt{\left(\frac{\delta\alpha}{\alpha}\right)^2 + \left(\frac{\delta t}{t^2}\right)^2} \tag{10}$$

1.1 Negligible sublimation rate

If $E_a \gg k_\mathbf{B}T$, then $\exp(-E_\mathrm{a}/k_\mathrm{B}T) \to 0$ and sublimation can be neglected in (9) and radiative cooling dominates:

$$\int_{T_0}^{T(t)}\frac{dT}{T^4} = -\frac{\sigma\varepsilon\pi d^2}{c_\mathrm{p}\rho V_\mathrm{hot}} = \int_0^t dt,$$

which can be easily integrated:

$$\frac{1}{T^3(t)} - \frac{1}{T_0^3} = \frac{3\sigma\varepsilon\pi d^2}{c_\mathrm{p}\rho V_\mathrm{hot}}t \tag{11}$$

If temperature data is fit to (11) by lumping all constants on the right-hand side to the slope:

$$s \equiv \frac{36\sigma\varepsilon d^2}{c_\mathrm{p}\rho\left[d^3 - (d - 2L_\mathrm{d})^3\right]} \tag{12}$$

We can solve for d to find the pebble diameter:

$$\begin{aligned}
sc_\mathrm{p}\rho\left[\cancel{d^3} - (\cancel{d^3} - 6d^2L_\mathrm{d} + 12dL_\mathrm{d}^2 - 8L_\mathrm{d}^3)\right] &= 36\sigma\varepsilon d^2 \\
sc_\mathrm{p}\rho\left(6d^2L_\mathrm{d} - 12dL_\mathrm{d}^2 + 8L_\mathrm{d}^3\right) - 36\sigma\varepsilon d^2 &= 0 \\
6(sc_\mathrm{p}\rho L_\mathrm{d} - 6\sigma\varepsilon)d^2 - 12sc_\mathrm{p}\rho L_\mathrm{d}^2 d + 8sc_\mathrm{p}\rho L_\mathrm{d}^3 &= 0
\end{aligned}$$

Which has the form

$$\begin{aligned}
d &= \frac{12sc_{\mathrm{p}}\rho L_{\mathrm{d}}^2 \pm \sqrt{(12sc_{\mathrm{p}}\rho L_{\mathrm{d}}^2)^2 - 192(sc_{\mathrm{p}}\rho L_{\mathrm{d}} - 6\sigma\varepsilon)(sc_{\mathrm{p}}\rho L_{\mathrm{d}}^3)}}{12(sc_{\mathrm{p}}\rho L_{\mathrm{d}} - 6\sigma\varepsilon)} \\
&= \frac{sc_{\mathrm{p}}\rho L_{\mathrm{d}}^2 \pm (sc_{\mathrm{p}}\rho L_{\mathrm{d}}^2)\sqrt{1 - 192\left[sc_{\mathrm{p}}\rho L_{\mathrm{d}} - 6\sigma\varepsilon)(sc_{\mathrm{p}}\rho L_{\mathrm{d}}^3)/(12sc_{\mathrm{p}}\rho L_{\mathrm{d}}^2)^2\right]}}{(sc_{\mathrm{p}}\rho L_{\mathrm{d}} - 6\sigma\varepsilon)} \\
&= \frac{sc_{\mathrm{p}}\rho L_{\mathrm{d}}^2 \pm (sc_{\mathrm{p}}\rho L_{\mathrm{d}}^2)\sqrt{1 - (4/3)(sc_{\mathrm{p}}\rho L_{\mathrm{d}} - 6\sigma\varepsilon)/(sc_{\mathrm{p}}\rho L_{\mathrm{d}})}}{(sc_{\mathrm{p}}\rho L_{\mathrm{d}} - 6\sigma\varepsilon)} \\
&= \frac{sc_{\mathrm{p}}\rho L_{\mathrm{d}}^2 \left[1 \pm \sqrt{1 - (4/3)(1 - 6\sigma\varepsilon/sc_{\mathrm{p}}\rho L_{\mathrm{d}})}\right]}{(sc_{\mathrm{p}}\rho L_{\mathrm{d}} - 6\sigma\varepsilon)} \\
&= L_{\mathrm{d}}\left(\frac{1 \pm \sqrt{1 - (4/3)(1 - 6\sigma\varepsilon/sc_{\mathrm{p}}\rho L_{\mathrm{d}})}}{(1 - 6\sigma\varepsilon/sc_{\mathrm{p}}\rho L_{\mathrm{d}})}\right),
\end{aligned}$$

which can be written as

$$\boxed{d = L_{\mathrm{d}}\left(\frac{1 \pm \sqrt{1 - 4/3\,\mathscr{C}}}{\mathscr{C}}\right), \quad \mathscr{C} = 1 - \frac{6\sigma\varepsilon}{sc_{\mathrm{p}}\rho L_{\mathrm{d}}}}. \tag{13}$$

For Eqn. (13) to be real

$$\mathscr{C} \leq \frac{3}{4}. \tag{14}$$

This means that, in order for d to be real, then

$$\frac{6\sigma\varepsilon}{sc_{\mathrm{p}}\rho L_{\mathrm{d}}} \geq \frac{1}{4} \tag{15}$$

To estimate the error of d, based on Eqn. (13), we need to estimate the partial derivatives:

$$\begin{aligned}
\frac{\partial d}{\partial s} &= \frac{\partial d}{\partial \mathscr{C}}\frac{\partial \mathscr{C}}{\partial s} = \frac{6\sigma\varepsilon}{s^2 c_{\mathrm{p}}\rho L_{\mathrm{d}}}\left(\frac{\partial d}{\partial \mathscr{C}}\right) \\
\frac{\partial d}{\partial c_{\mathrm{p}}} &= \frac{\partial d}{\partial \mathscr{C}}\frac{\partial \mathscr{C}}{\partial c_{\mathrm{p}}} = \frac{6\sigma\varepsilon}{sc_{\mathrm{p}}^2\rho L_{\mathrm{d}}}\left(\frac{\partial d}{\partial \mathscr{C}}\right) \\
\frac{\partial d}{\partial \rho} &= \frac{\partial d}{\partial \mathscr{C}}\frac{\partial \mathscr{C}}{\partial \rho} = \frac{6\sigma\varepsilon}{sc_{\mathrm{p}}\rho^2 L_{\mathrm{d}}}\left(\frac{\partial d}{\partial \mathscr{C}}\right) \\
\frac{\partial d}{\partial L_{\mathrm{d}}} &= \frac{\partial d}{\partial \mathscr{C}}\frac{\partial \mathscr{C}}{\partial L_{\mathrm{d}}} = \frac{6\sigma\varepsilon}{sc_{\mathrm{p}}\rho L_{\mathrm{d}}^2}\left(\frac{\partial d}{\partial \mathscr{C}}\right)
\end{aligned}$$

and

$$\frac{\partial d}{\partial \mathscr{C}} = L_{\mathrm{d}}\left(\frac{\mp 4/3\,\mathscr{C}\,(1 - 4/3\,\mathscr{C})^{-1/2} - 1 \mp (1 - 4/3\,\mathscr{C})^{1/2}}{\mathscr{C}^2}\right)$$

1.2 Negligible radiative cooling

If the emissivity $\varepsilon \to 0$, then only the sublimation cooling is important. In such case:

$$-c_{\mathrm{p}}\rho V_{\mathrm{hot}}\frac{dT}{dt} = \frac{Hr_0}{N_{\mathrm{A}}}\exp\left(-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right) \tag{16}$$

Integration of Eqn. (16) requires the use of the exponential integral $\mathrm{Ei}(x)$:

$$-c_\mathrm{p}\rho V_\mathrm{hot}\int_{T_0}^{T(t)} \exp\left(\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right) dT = -c_\mathrm{p}\rho V_\mathrm{hot}\left[T\exp\left(\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right) - \frac{E_\mathrm{a}}{k_\mathrm{B}}\mathrm{Ei}\left(\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right)\right]_{T_0}^{T(t)} = \frac{Hr_0}{N_\mathrm{A}}\int_0^t dt = \frac{Hr_0}{N_\mathrm{A}}t \tag{17}$$

where

$$\mathrm{Ei}(x) = -\int_{-x}^{\infty}\frac{e^{-t}dt}{t} = \int_{\infty}^{x}\frac{e^{t}dt}{t} \tag{18}$$

The temperature of the free pebble at time t can be obtained from Eqn. (17) by finding the roots to

$$f_\mathrm{subl} \equiv c_\mathrm{p}\rho V_\mathrm{hot}\left[T_0\exp\left(\frac{E_\mathrm{a}}{k_\mathrm{B}T_0}\right) - T\exp\left(\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right) - \frac{E_\mathrm{a}}{k_\mathrm{B}}\mathrm{Ei}\left(\frac{E_\mathrm{a}}{k_\mathrm{B}T_0}\right) + \frac{E_\mathrm{a}}{k_\mathrm{B}}\mathrm{Ei}\left(\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right)\right] - \frac{Hr_0}{N_\mathrm{A}}t \tag{19}$$

For glassy carbon $\kappa = (6.60 \pm 0.18)\times 10^{-2}\,\mathrm{W/cm\text{-}K}$, $c_\mathrm{p} = (0.714 \pm 0.022)\,\mathrm{J/g\text{-}K}$ (Shinzato and Baba[2]), and $\rho = (1.372 \pm 0.003)\,\mathrm{g/cm^3}$ (measured). Using $\alpha = \kappa/\rho c_\mathrm{cp}$. Then $\alpha = (0.067 \pm 0.003)\,\mathrm{cm^2/s}$, Where the error on α was estimated by Eqn.

$$\delta\alpha = \alpha\sqrt{\left(\frac{\delta\kappa}{\kappa}\right)^2 + \left(\frac{\delta\rho}{\rho}\right)^2 + \left(\frac{\delta c_\mathrm{p}}{c_\mathrm{p}}\right)^2}$$

Glassy carbon pebbles with average $d = 0.09\,\mathrm{cm}$ are observed to remain in the beam path for $\approx 0.25\,\mathrm{s}$ and they typically reach $\approx 2500\,^\circ\mathrm{C}$ in about $0.1\,\mathrm{s}$. If we consider $t_\mathrm{ex} \approx 0.1\,\mathrm{s}$, then $L_\mathrm{d} \approx 0.082\,\mathrm{mm}$

1.3 Sublimation and radiation

Integration of Eqn. (9) needs to be solved numerically:

$$-c_\mathrm{p}\rho V_\mathrm{hot}\int_{T_0}^{T(t)}\frac{1}{\sigma\varepsilon AT^4 + H_\mathrm{s}\frac{r_0}{N_\mathrm{A}}\exp\left(-\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right)}dT = c_\mathrm{p}\rho V_\mathrm{hot}\int_{T(t)}^{T_0}\frac{1}{\pi\sigma\varepsilon d^2T^4 + H_\mathrm{s}\frac{r_0}{N_\mathrm{A}}\exp\left(-\frac{E_\mathrm{a}}{k_\mathrm{B}T}\right)}dT = t \tag{20}$$

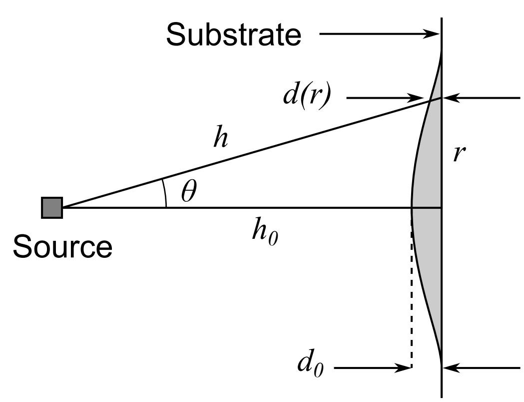

Figure 1: Schematic of geometry of evaporation (adapted from de Matos Loureiro da Silva Pereira *et al.*[3])

2 Carbon deposition kinetics

Fig. 2 shows the thickness profile of the carbon deposit due to the sublimation of carbon from the pebble rod subject to high heat loads. The coordinate r is measured from the axis of the laser beam. The experimental data is fitted to the cosine law (de Matos Loureiro da Silva Pereira *et al.*[3] and references therein):

$$\frac{d}{d_0} = \frac{h_0^2}{h^2}\cos^n\theta, \tag{21}$$

where d is the coating thickness at a distance h from the source, d_0 is the thickness directly over the vapor flux at a distance h_0 from the source, θ is the angle from the normal to the source to point in the substrate at a distance r from the axis of the beam, and n is a coefficient that defines the focus of the source. Furthermore,

$$h = \sqrt{h_0^2 + r^2}, \quad \cos\theta = \frac{h_0}{h}.$$

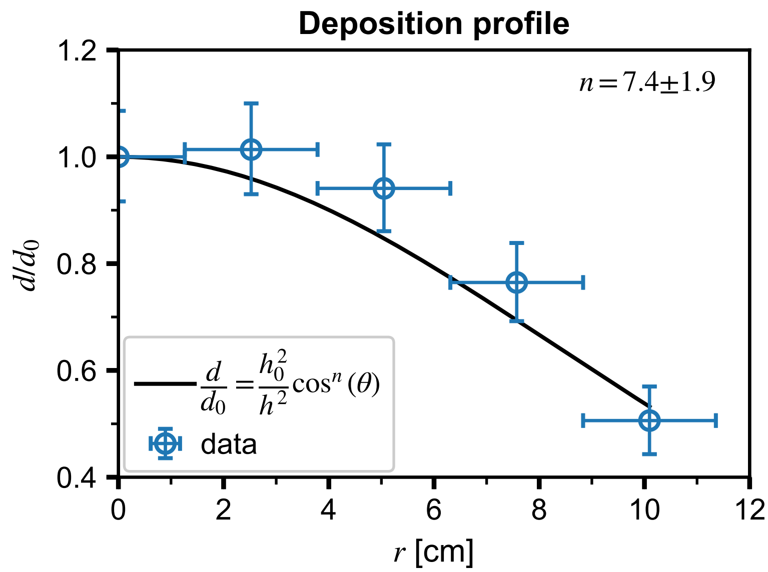

Figure 2: Thickness profile of the carbon film deposited around the axis of the heating beam.

In other words, Eqn. (21) can be expressed in terms of r as

$$\frac{d}{d_0} = \frac{h_0^{n+2}}{(h_0^2 + r^2)^{(n+2)/2}}, \tag{22}$$

The distance from the source to the substrate is $h_0 = 27\,\text{cm}$.
The volume of the deposit is obtained by integration of Eqn. (22) in cylindrical polar coordinates:

$$\begin{aligned} V &= -\int_0^{2\pi}\int_0^{\infty}\left(\frac{d_0 h_0^{n+2}}{(h_0^2+r^2)^{(n+2)/2}}\right) r dr d\theta \\ &= -d_0 h_0^{n+2}\int_0^{2\pi}\int_0^{\infty}\left(\frac{r}{(h_0^2+r^2)^{(n+2)/2}}\right) dr d\theta. \end{aligned} \tag{23}$$

Define $u \equiv h_0^2 + r^2 \to du = 2rdr$, and plug it into Eqn. (23):

$$\begin{aligned} V &= -\lim_{\xi\to\infty}\frac{d_0 h_0^{n+2}}{2}\int_0^{2\pi}\int_{h_0^2}^{h_0^2+\xi^2} u^{-(n+2)/2} du d\theta \\ &= -\lim_{\xi\to\infty}\frac{d_0 h_0^{n+2}}{2}\int_0^{2\pi}\left.\frac{u^{-n/2}}{-n/2}\right|_{h_0^2}^{h_0^2+\xi^2} d\theta \\ &= \frac{d_0 h_0^{n+2}}{n}\int_0^{2\pi}\lim_{\xi\to\infty}\left[\frac{1}{h_0^n} - \frac{1}{\left(h_0^2+\xi^2\right)^{n/2}}\right] d\theta \end{aligned} \tag{24}$$

The volume of the deposit is then given by

$$\boxed{V = \frac{2\pi d_0 h_0^2}{n}} \tag{25}$$

The average deposit rate in mol/s is given by

$$r_{\text{deposit}} = 2\pi\rho \frac{h_0^2}{nM_{\text{C}}} \left(\frac{d_0}{\Delta t_{\text{laser}}} \right), \tag{26}$$

where $M_{\text{C}} = 12.011\,\text{g/mol}$ is the molar mass of carbon, and t_{laser} is the laser emission time.

Consider 1 Torr-L at $T = 298\,\text{K}$ in an ideal gas:

$$PV = Nk_{\text{B}}T \Rightarrow N = \frac{(133.322\,\text{N/m}^2)(10^{-3}\,\text{m}^3)}{k_{\text{B}}(298\,\text{K})} = 5.381 \times 10^{-5}\,\text{mol of C} = 3.240 \times 10^{19}\,\text{C atoms}$$

Considering a density of $\rho_{\text{film}} = 2.2\,\text{g/cm}^3$ (Kumar *et al.*[4]), the evaporation rate in Torr-L/s is

$$r_{\text{ev}} = 2\pi\rho \frac{h_0^2}{nM_{\text{C}}} \left(\frac{d_0}{\Delta t_{\text{laser}}} \right) \times \left(\frac{1 \text{ Torr-L}}{5.381 \times 10^{-5}\,\text{mol}} \right) = 21.388 \times 10^3\,\text{Torr-L/cm}^3 \left(\frac{h_0^2}{n} \right) \left(\frac{d_0}{\Delta t_{\text{laser}}} \right) \tag{27}$$

Order of magnitude analysis: d_0 is on the order of $100\,\text{nm} \to 100 \times 10^{-7}\,\text{cm} \to 10^{-5}\,\text{cm}$. $h_0 \approx 27\,\text{cm}$ and $n \approx 7.5$, and $\Delta t_{\text{laser}} \sim 0.5\,\text{s}$ so that

$$r_{\text{ev}} \sim 40\,\text{Torr-L/s} = 2.8 \times 10^{20}\,\text{C atoms/s}$$

For a sample of diameter $d = 1\,\text{cm} \to A \approx 1\,\text{cm}^2 \times (1\text{ m}/(10^2\text{ cm})^2 = 1 \times 10^{-4}\,\text{m}^2$

$$r_{\text{ev}} \sim 400 \times 10^4\,\text{Torr-L/s/m}^2$$

Note: The previous analysis does not take into account the re-deposition of carbon on the source.

References

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