Mathematical methods in chemistry: Part I

Lecture 1: Laplace transform

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Outline

- Why should one study Laplace transforms in physical chemistry and chemical engineering?
- Definition and basic properties of the Laplace transform
- Heaviside function
- Inverse Laplace transform

Why study Laplace transforms?

(1) **Chemical kinetics**:

Given initial concentrations of A, B, C,…, what are their concentrations at time t?

Examples:

(a) Reversible reaction:

(b) Consecutive reaction:

Why study Laplace transforms?

(2) **Molecular dynamics** (e.g., vibrations)

Given initial positions $\boldsymbol{r}_j(0)$ and velocities $\boldsymbol{v}_j(0)$ of atoms, what are their positions $\boldsymbol{r}_j(t)$ and velocities $\boldsymbol{v}_j(t)$ at time t?

Why study Laplace transforms?

(3) **Chemical engineering** (solve **partial differential equations**)

What is the temperature dependence on position $\boldsymbol{r}$ and time t in a material or reaction vessel?

Definition of the Laplace transform

Definition: $F(s)$ is a Laplace transform of $f(t)$ and we write $\mathcal{L}[f(t)] = F(s)$ if

$$F(s) \coloneqq \int_0^\infty f(t)\mathrm{e}^{-st}\,\mathrm{d}t.$$

This defines a mapping $\mathcal{L}: f(t) \mapsto F(s)$. Note that $f(t)$ has to be a "suitable" function so that the integral is well defined. This is so, e.g., if $f(t)$ is of "exponential order," i.e., if there are positive constants C and M such that

$$|f(t)| \leq C\mathrm{e}^{Mt} \quad \text{for all } t \geq 0.$$

Example 1: $f(t) = 1$.

$$F(s) = \mathcal{L}[f(t)] = \int_0^\infty 1 \cdot \mathrm{e}^{-st}\,\mathrm{d}t = -\frac{\mathrm{e}^{-st}}{s}\bigg|_0^\infty = \frac{1}{s}$$

Basic properties of the Laplace transform

(1) Linearity: $\mathcal{L}[af(t) + bg(t)] = a\mathcal{L}[f(t)] + b\mathcal{L}[g(t)]$

Proof: Using the linearity of the integral, we have

$$\text{LHS} = \int_0^\infty [af(t) + bg(t)]\mathrm{e}^{-st}\,\mathrm{d}t$$

$$= a\int_0^\infty f(t)\mathrm{e}^{-st}\,\mathrm{d}t + b\int_0^\infty g(t)\mathrm{e}^{-st}\,\mathrm{d}t = \text{RHS}$$

(Note that one should also prove the existence of the LHS.)

Example 2: Laplace transform of $\sin t$, $\cos t$:

Use a trick—recall that $\mathrm{e}^{\mathrm{i}t} = \cos t + \mathrm{i}\sin t$ and linearity:

$$\mathcal{L}[\cos t] + \mathrm{i}\mathcal{L}[\sin t] = \mathcal{L}[\mathrm{e}^{\mathrm{i}t}] = \int_0^\infty \mathrm{e}^{\mathrm{i}t}\mathrm{e}^{-st}\,\mathrm{d}t = \frac{\mathrm{e}^{(\mathrm{i}-s)t}}{\mathrm{i}-s}\bigg|_0^\infty = \frac{1}{s-\mathrm{i}}$$

$$= \frac{s+\mathrm{i}}{(s-\mathrm{i})(s+\mathrm{i})} = \frac{s+\mathrm{i}}{s^2+1} = \frac{s}{s^2+1} + \frac{\mathrm{i}}{s^2+1}$$

Basic properties of the Laplace transform

(2) $\mathcal{L}[t^n f(t)] = (-1)^n \frac{\mathrm{d}^n}{\mathrm{d}s^n}F(s)$

Proof by induction:

(a) For $n = 0$, $\mathcal{L}[f(t)] = F(s)$ is just the definition of LT.

(b) Assume that the claim holds for $n = k$, i.e., $\mathcal{L}[t^k f(t)] = (-1)^k\,\mathrm{d}^k F(s)/\,\mathrm{d}s^k$. Let us prove it for $n = k+1$:

$$\mathcal{L}[t^{k+1}f(t)] = \int_0^\infty t^{k+1}f(t)\mathrm{e}^{-st}\,\mathrm{d}t = -\frac{\mathrm{d}}{\mathrm{d}s}\int_0^\infty t^k f(t)\mathrm{e}^{-st}\,\mathrm{d}t$$

$$= -\frac{\mathrm{d}}{\mathrm{d}s}\mathcal{L}[t^k f(t)] = -\frac{\mathrm{d}}{\mathrm{d}s}(-1)^k\frac{\mathrm{d}^k}{\mathrm{d}s^k}F(s) = (-1)^{k+1}\frac{\mathrm{d}^{k+1}}{\mathrm{d}s^{k+1}}F(s).$$

where we used the relation $\frac{\mathrm{d}}{\mathrm{d}s}\mathrm{e}^{-st} = -t\mathrm{e}^{-st}$ in the second step and the induction assumption in the penultimate step.

Basic properties of the Laplace transform

Example 3: $f(t) = t^n$

$$\mathcal{L}[t^n] = \mathcal{L}[t^n \cdot 1] = (-1)^n \frac{d^n}{ds^n}\mathcal{L}[1] = (-1)^n \frac{d^n}{ds^n}\frac{1}{s}$$

$$= \frac{(-1)^n(-1)^n}{s^{n+1}} 1 \cdot 2 \cdot \cdots \cdot n = \frac{n!}{s^{n+1}}$$

(3) First shift theorem: $\mathcal{L}[\mathrm{e}^{-bt} f(t)] = F(s+b)$

Proof: LHS = $\int_0^\infty \mathrm{e}^{-st}\mathrm{e}^{-bt} f(t)\,\mathrm{d}t = \int_0^\infty \mathrm{e}^{-(s+b)t} f(t)\,\mathrm{d}t$ = RHS.

Example 4: $g(t) = t^n \mathrm{e}^{at}$

$\mathcal{L}[t^n \mathrm{e}^{at}] = \mathcal{L}[\mathrm{e}^{at} f(t)] = F(s-a) = \frac{n!}{(s-a)^{n+1}}$

Exercise: Derive it from $\mathcal{L}[t^n \mathrm{e}^{at}] = \mathcal{L}[t^n f(t)]$ with $f(t) = e^{at}$.

Basic properties of the Laplace transform

(4) Change of scale: $\mathcal{L}[f(at)] = \frac{1}{a} F\left(\frac{s}{a}\right)$

Proof is an exercise.

Example 5: $g(t) = \sin(\omega t)$

Note that $g(t) = f(\omega t)$, where $f(t) = \sin t$.

$$\mathcal{L}[\sin(\omega t)] = \frac{1}{\omega} F\left(\frac{s}{\omega}\right) = \frac{1}{\omega}\frac{1}{\left(\frac{s}{\omega}\right)^2 + 1} = \frac{\omega}{s^2 + \omega^2}$$

Basic properties of the Laplace transform

(5) Laplace transform of a derivative

$$\mathcal{L}\left[\frac{\mathrm{d}^n}{\mathrm{d}t^n} f(t)\right] = s^n F(s) - s^{n-1} f(0) - s^{n-2} f'(0) - \cdots - f^{(n-1)}(0)$$

Proof by induction:

(a) $n = 0$: $\mathcal{L}[f(t)] = F(s)$ is the definition of the LT.

(b) Assume the claim holds for $n = k$. Let's prove it for $n = k+1$:

LHS = $\mathcal{L}\left[\frac{d^{k+1}}{\mathrm{d}t^{k+1}} f(t)\right] = \int_0^\infty f^{(k+1)}(t)\mathrm{e}^{-st}\,\mathrm{d}t = f^{(k)}(t)\mathrm{e}^{-st}\big|_0^\infty + \int_0^\infty f^{(k)}(t) s \mathrm{e}^{-st}\,\mathrm{d}t = -f^{(k)}(0) + s\mathcal{L}\left[f^{(k)}(t)\right] = -f^{(k)}(0) + s\left[s^k F(s) - s^{k-1} f(0) - \cdots - f^{(k-1)}(0)\right] = s^{k+1} F(s) - s^k f(0) - \cdots - f^{(k)}(0)$ = RHS

Basic properties of the Laplace transform

Example 6: $\mathcal{L}[f'(t)] = sF(s) - f(0)$

$\mathcal{L}[f''(t)] = s^2 F(s) - sf(0) - f'(0)$

LT of a derivative is extremely important in chemical kinetics because it transforms **linear differential equations** to **algebraic equations**.

Example 7: If $f(t) = \sin(\omega t)$ then, by ex. 5, $F(s) = \frac{\omega}{s^2+\omega^2}$.

Also, $f'(t) = \omega\cos(\omega t)$ and, by ex. 6,

$$\mathcal{L}[\omega\cos(\omega t)] = \mathcal{L}[f'(t)] = sF(s) - f(0) = s\frac{\omega}{s^2+\omega^2} - 0$$

Hence $\mathcal{L}[\cos(\omega t)] = \frac{s}{s^2+\omega^2}$.

Basic properties of the Laplace transform

(6) Laplace transform of an integral: $\mathcal{L}\left[\int_0^t f(u)\,\mathrm{d}u\right] = \frac{F(s)}{s}$

Proof: Define $g(t) := \int_0^t f(u)\,\mathrm{d}u$. Then $g(0) = 0$, $g'(t) = f(t)$.

$$F(s) = \mathcal{L}[f(t)] = \mathcal{L}[g'(t)] = sG(s) - g(0) = sG(s)$$

Hence $G(s) = \frac{F(s)}{s}$, QED.

(7) If $\mathcal{L}\left[\frac{f(t)}{t}\right] \to 0$ as $s \to \infty$, then $\mathcal{L}\left[\frac{f(t)}{t}\right] = \int_s^\infty F(u)\,\mathrm{d}u$.

Proof: Define $g(t) := f(t)/t$, use (2) and integrate from s to ∞:

$$F(s) = \mathcal{L}[f(t)] = \mathcal{L}[tg(t)] = -\frac{\mathrm{d}}{\mathrm{d}s}\mathcal{L}[g(t)] = -\frac{\mathrm{d}}{\mathrm{d}s}\mathcal{L}\left[\frac{f(t)}{t}\right]$$

$$\int_s^\infty F(u)\,\mathrm{d}u = -\mathcal{L}\left[\frac{f(t)}{t}\right]\Bigg|_s^\infty = \mathcal{L}\left[\frac{f(t)}{t}\right]\Bigg|_s = \mathcal{L}\left[\frac{f(t)}{t}\right]$$

Basic properties of the Laplace transform

Example 8: Find LT of $\operatorname{sinc} t := (\sin t)/t$.

Define $f(t) := \sin t$ and use (7) with $F(s) = \frac{1}{s^2+1}$.

$$\mathcal{L}\left[\frac{\sin t}{t}\right] = \int_s^\infty \frac{\mathrm{d}u}{u^2+1} = \operatorname{arctg} u\Big|_s^\infty = \frac{\pi}{2} - \operatorname{arctg} s = \operatorname{arctg}\frac{1}{s}$$

Example 9: Find LT of the **sine integral** $\mathrm{Si}(t) := \int_0^t \frac{\sin u}{u}\,\mathrm{d}u$.

Define $f(t) = (\sin t)/t$ and use (6) and Ex. 8:

$$\mathcal{L}[\mathrm{Si}(t)] = \frac{F(s)}{s} = \frac{1}{s}\operatorname{arctg}\frac{1}{s}$$

Heaviside function

Heaviside step function is defined by:

$h(t) = 0$ for $t < 0$,

$h(t) = 1$ for $t \geq 0$.

Laplace transform: $\mathcal{L}[h(t)] = \mathcal{L}[1] = \frac{1}{s}$

Shifted Heaviside function:

$h(t - t_0) = 0$ for $t < t_0$,

$h(t - t_0) = 1$ for $t \geq t_0$.

Exercise: Find $\mathcal{L}[h(t - t_0)]$ for $t_0 \geq 0$.

Interpretation: $h(t - t_0)f(t)$ "turns on" $f(t)$ at time t_0

Second shift theorem

(8) Second shift theorem: $\mathcal{L}[h(t - t_0)f(t - t_0)] = \mathrm{e}^{-st_0}F(s)$ (if $t_0 \geq 0$).

Proof: LHS = $\int_0^\infty h(t - t_0)f(t - t_0)\mathrm{e}^{-st}\,\mathrm{d}t$

$$= \int_{t_0}^\infty f(t - t_0)\mathrm{e}^{-st}\,\mathrm{d}t = \int_0^\infty f(u)\mathrm{e}^{-s(t_0+u)}\,\mathrm{d}u = \text{RHS},$$

where we used the definition of h and substitution $u = t - t_0$.

Inverse Laplace transform

Definition: If $F(s)$ is the Laplace transform of $f(t)$, $F(s) = \mathcal{L}[f(t)]$, then $f(t)$ is said to be the **inverse Laplace transform** of $F(s)$ and we write $\mathcal{L}^{-1}[F(s)] = f(t)$.

Properties of the inverse Laplace transform: $\mathcal{L}^{-1}[F(s)]$:

1) is **linear**,
2) is **unique** (up to "null'' functions $n(t)$ for which $\mathcal{L}[n(t)] = 0$),
3) **may not exist**; a necessary condition: $F(s) \to 0$ for $s \to \infty$, (unless we use "*generalized functions*," see next lecture)
4) can be **hard to find**.

Inverse Laplace transforms

Example 10: $F(s) = \frac{s-1}{s^2+2s-8}$, what is $\mathcal{L}^{-1}[F(s)]$?

Partial fractions: $F(s) = \frac{s-1}{(s+4)(s-2)} = \frac{a}{s+4} + \frac{b}{s-2}$, $a = \frac{5}{6}$, $b = \frac{1}{6}$.

Linearity: $\mathcal{L}^{-1}[F(s)] = a\mathcal{L}^{-1}\left[\frac{1}{s+4}\right] + b\mathcal{L}^{-1}\left[\frac{1}{s-2}\right]$

Shift theorem:

$\mathcal{L}^{-1}[F(s)] = a\mathrm{e}^{-4t}\mathcal{L}^{-1}\left[\frac{1}{s}\right] + b\mathrm{e}^{2t}\mathcal{L}^{-1}\left[\frac{1}{s}\right] = \frac{5}{6}\mathrm{e}^{-4t} + \frac{1}{6}\mathrm{e}^{2t}$,

where we used $\mathcal{L}[1] = \frac{1}{s}$ in the last step.

Inverse Laplace transforms

Example 11: $F(s) = \frac{s}{s^2+6s+9}$, what is $\mathcal{L}^{-1}[F(s)]$?

Partial fractions: $F(s) = \frac{s}{(s+3)^2} = \frac{1}{s+3} - \frac{3}{(s+3)^2}$.

Linearity: $\mathcal{L}^{-1}[F(s)] = \mathcal{L}^{-1}\left[\frac{1}{s+3}\right] - 3\mathcal{L}^{-1}\left[\frac{1}{(s+3)^2}\right]$

Shift theorem:

$\mathcal{L}^{-1}[F(s)] = \mathrm{e}^{-3t}\mathcal{L}^{-1}\left[\frac{1}{s}\right] - 3\mathrm{e}^{-3t}\mathcal{L}^{-1}\left[\frac{1}{s^2}\right] = \mathrm{e}^{-3t}(1-3t)$,

where we used $\mathcal{L}[1] = \frac{1}{s}$ and $\mathcal{L}[t] = \frac{1}{s^2}$ in the last step.

Inverse Laplace transforms

Example 12: $F(s) = \frac{a}{s^2-a^2}$, what is $\mathcal{L}^{-1}[F(s)]$?

Partial fractions: $F(s) = \frac{a}{(s+a)(s-a)} = \frac{1/2}{s-a} - \frac{1/2}{s+a}$.

Linearity: $\mathcal{L}^{-1}[F(s)] = \frac{1}{2}\mathcal{L}^{-1}\left[\frac{1}{s-a}\right] - \frac{1}{2}\mathcal{L}^{-1}\left[\frac{1}{s+a}\right]$

Shift theorem (3) and/or ex. 4:

$\mathcal{L}^{-1}[F(s)] = \frac{1}{2}(\mathrm{e}^{at} - \mathrm{e}^{-at})\mathcal{L}^{-1}\left[\frac{1}{s}\right] = \frac{1}{2}(\mathrm{e}^{at} - \mathrm{e}^{-at}) = \sinh(at)$.

Limiting theorems

If you do not know $F(s)$ explicitly, it is nice to know its behavior for large or small values of s.

(9) Initial value theorem: $f(0) = \lim_{s\to\infty} sF(s)$

Proof: We know that $sF(s) - f(0) = \mathcal{L}[f'(t)]$. Assuming that f' is of exponential order, $|f'(t)| \le C\mathrm{e}^{Mt}$, we have:

$|\mathcal{L}[f'(t)]| = \left|\int_0^\infty \mathrm{e}^{-st} f'(t)\,\mathrm{d}t\right| \le \int_0^\infty |\mathrm{e}^{-st} f'(t)|\,\mathrm{d}t \le$
$C\int_0^\infty \mathrm{e}^{-st}\mathrm{e}^{Mt}\,\mathrm{d}t = -\frac{C}{M-s} \to 0$ as $s \to \infty$,

hence

$$\lim_{s\to\infty}[sF(s) - f(0)] = 0.$$

Limiting theorems

(10) Final value theorem: $\lim_{t\to\infty} f(t) = \lim_{s\to 0} sF(s)$ if the limits exist.

Proof: See the book by Dyke.

Example 13: $f(t) = \mathrm{e}^{-t} \Rightarrow F(s) = \mathcal{L}[f(t)] = \frac{1}{s+1}$

Check (9):

$$\mathrm{e}^{-t}|_{t=0} = 1 = \lim_{s\to\infty} \frac{s}{1+s}$$

Check (10):

$$\lim_{t\to\infty} \mathrm{e}^{-t} = 0 = \lim_{s\to 0} \frac{s}{1+s}$$