Physical kinetics seminar

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1.5 Eigenfunction Expansion and the Resolvent

1.5.1 Liouville equation integrating factor

Let us remember the Liouville equation

$$\frac{\partial D}{\partial t} = -i \hat{\Lambda} D$$

For time-independent $\hat{\Lambda}$ (that is, H without explicit time-dependence) we have formal solution

$$D(q, p, t) = e^{-i\hat{\Lambda} t} D(q, p, 0)$$

with operator $e^{-i\hat{\Lambda}t}$ being defined by its Taylor series expansion

$$e^{-i\hat{\Lambda} t} = 1 - it\hat{\Lambda} + \frac{(-it)^2}{2}\hat{\Lambda}^2 + \dots$$

Remembering that $\hat{\Lambda} = i[H, \ ]$ we obtain

$$D(q,p,t) = \left\{ 1 + t[H, \ ] + \frac{t^2}{2}[H,[H, \ ]] + \dots \right\} D(q,p,0)$$

This is the same as we had by doing Taylor series expansion of $D(q,p,t)$.

If $\hat{\Lambda}$ is time-dependent, $\hat{\Lambda}(t)$, then the formal solution of the Liouville equation is

$$D(q,p,t) = \hat{T}_+ e^{-i\int_0^t dt' \hat{\Lambda}(t')} D(q,p,0)$$

with $\hat{T}_+$ being the chronological time-ordering operator, defined by

$$\hat{T}_+ (\hat{A}(t_1)\hat{B}(t_2)) = \begin{cases} \hat{A}(t_1)\hat{B}(t_2), & t_1 > t_2 \\ \hat{B}(t_2)\hat{A}(t_1), & t_2 > t_1 \end{cases}$$

Now let us see how our formal solution can help us in actual calculations.

For now we assume ~~the~~ time-independent $\hat{\Lambda}$, and we further assume that we know the eigenvalues and eigenfunctions:

$$\hat{\Lambda} \varphi_n = \omega_n \varphi_n$$

Now we say that the set $\{\varphi_n\}$ span the (Hilbert) space that contains $D(q, p, 0)$. Then we can write

$$D_0(q, p) = \sum_{\forall n} D_n \varphi_n$$

Assuming that the eigenfunctions are orthonormal, the coefficients can be expressed as

$$D_n = \langle \varphi_n | D_0(q, p) \rangle = \int dq\, dp\, \varphi_n^* D_0$$

With this, the solution to the Liouville equation is expressed as

$$D(q, p, t) = e^{-i\hat{\Lambda}t} \sum_{\forall n} D_n \varphi_n = \sum_{\forall n} e^{-i\omega_n t} D_n \varphi_n$$

1.5.2 Example: The Ideal Gas

Now we will use our obtained expression to find the solution to the Liouville equation for a collection of N noninteracting molecules, that is, an ideal gas.

We will assume the gas to be confined to a large cubical box with L being its edge length.

The Hamiltonian is

$$H = \sum_{s=1}^{N} \frac{\vec{p}_s^{\,2}}{2m} \quad \Big] \leftarrow \text{here we use Cartesian vectors}$$

while the positions are confined $0 \le x_s^{(j)} \le L$, with $x_s^{(j)}$ being a Cartesian component of $\vec{x}_s$.

We will denote the Liouville operator by $\hat{\Lambda}_0$. We have

$$\hat{\Lambda}_0 = -i \sum_s \sum_j \frac{\partial H}{\partial p_s^{(j)}} \frac{\partial}{\partial x_s^{(j)}} = -i \sum_s \nabla_{\vec{p}_s} H \cdot \nabla_{\vec{x}_s} = -i \sum_s \frac{\partial H}{\partial \vec{p}_s} \cdot \frac{\partial}{\partial \vec{x}_s} = -i \sum_s \vec{v}_s \cdot \frac{\partial}{\partial \vec{x}_s}$$

Here we use notation

$$\frac{\partial}{\partial \vec{a}} = \nabla_{\vec{a}}$$

Also we have $\vec{v}_s = \frac{\vec{p}_s}{m}$

The eigenvalue equation will be

$$\hat{\Lambda}_0 \psi_n = \omega_n \psi_n \quad \Rightarrow \quad -i \sum_s \vec{v}_s \cdot \frac{\partial}{\partial \vec{x}_s} \psi_n = \omega_n \psi_n$$

We will assume the trial solution to be of the form

$$\psi_{(\vec{k})} = A \exp\left(i \sum_s \vec{k}_s \cdot \vec{x}_s\right) \quad , \quad (\vec{k}) = (\vec{k}_1, \dots, \vec{k}_N)$$

Then

$$-i \sum_s \vec{v}_s \cdot \frac{\partial}{\partial \vec{x}_s} \psi_{(\vec{k})} = -i A \sum_s \vec{v}_s \cdot \frac{\partial}{\partial \vec{x}_s} \exp\left(i \sum_{s'} \vec{k}_{s'} \cdot \vec{x}_{s'}\right) =$$

$$= -i A \sum_s \vec{v}_s \cdot i \vec{k}_s \exp\left(i \sum_{s'} \vec{k}_{s'} \cdot \vec{x}_{s'}\right)$$

From here

$$\omega_{(\vec{k})} = \sum_s \vec{v}_s \cdot \vec{k}_s$$

If we assume periodic boundary conditions [Exercise 1.17]
we must have

$$A \exp\left(i \sum_s \vec{k}_s \cdot \vec{x}_s\right) = A \exp\left(i \sum_s \vec{k}_s \cdot (\vec{x}_s + \vec{L})\right) \quad , \text{ with } \vec{L} = L(1,1,1)$$

This will be satisfied if

$$\exp\left(i \sum_s \vec{k}_s \cdot \vec{L}\right) = 1 \quad \Rightarrow k_s^{(j)} \cdot L = 2\pi n_s^{(j)}$$

$$\Rightarrow \vec{k}_s = \frac{2\pi}{L} \vec{n}_s \quad , \quad \text{with } n_s^{(j)} \text{ being integers}$$

From normalization we have

$$|A|^2 \int dq \; e^{i \sum_s \vec{k}_s \cdot \vec{x}_s} \; e^{-i \sum_s \vec{k}_s \cdot \vec{x}_s} = 1$$

$$\Rightarrow |A|^2 L^{3N} = 1$$

$$\Rightarrow A = \frac{1}{L^{3N/2}}$$

We finally have

$$\psi_{(\vec{k})} = \frac{1}{L^{3N/2}} \exp\left(i \sum_s \vec{k}_s \cdot \vec{x}_s\right)$$

Thus, the solution to the Liouville equation is

$$D(\vec{x}^N, \vec{p}^N, t) = \sum_{(\vec{k})} D_{(\vec{k})}(\vec{p}^N)\, \psi_{(\vec{k})}(\vec{x}^N)\, e^{-i\omega_{(\vec{k})} t}$$

with $\vec{x}^N$ and $\vec{p}^N$ representing $3N$-dimensional vectors

The initial condition can be written as

$$D_0(\vec{x}^N, \vec{p}^N) = \sum_{(\vec{k})} D_{(\vec{k})}(\vec{p}^N)\, \psi_{(\vec{k})}(\vec{x}^N)$$

From here we can obtain the expansion coefficients

$$D_{(\vec{k})}(\vec{p}^N) = \langle \psi_{(\vec{k})} | D_0(\vec{x}^N, \vec{p}^N) \rangle = \frac{1}{L^{3N/2}} \int d\vec{x}^N \exp\left(-i \sum_s (\vec{k}_s \cdot \vec{x}_s)\right) D_0(\vec{x}^N, \vec{p}^N)$$

Finally, our solution becomes

$$D(\vec{x}^N, \vec{p}^N, t) = \frac{1}{L^{3N/2}} \sum_{(\vec{k})} D_{(\vec{k})}(\vec{p}^N) \exp\left[i \sum_s \vec{k}_s \cdot (\vec{x}_s - \vec{v}_s t)\right]$$

Thus, our solution is a function of $2 \times (3N)$ constants of motion

$$\{\vec{p}_s, \vec{x}_s - \vec{v}_s t\}$$

1.5.3 Free-Particle Propagator

We again consider the free-particle Hamiltonian and the corresponding Liouville operator. The formal solution to the Liouville equation is

$$D(x, v, t) = e^{-i\hat{\Lambda}_0 t} D(x, v, 0)$$

with

$$i\hat{\Lambda}_0 t = -\sum_s t \vec{v}_s \cdot \frac{\partial}{\partial \vec{x}_s}$$

Since the particles are independent, the factors in $e^{-i\hat{\Lambda}_0 t}$ commute.

Consider the evolution of a single particle

$$D(\vec{x}_1, \vec{v}_1, t) = \exp\left(-t \vec{v}_1 \cdot \frac{\partial}{\partial \vec{x}_1}\right) D(\vec{x}_1, \vec{v}_1, 0)$$

Expanding the exponential gives

$$\exp\left(-t\,\vec{v}_1\cdot\frac{\partial}{\partial\vec{x}_1}\right) D(\vec{x}_1,\vec{v}_1,0) =$$

$$= \left[1 - t\,\vec{v}_1\cdot\frac{\partial}{\partial\vec{x}_1} + \frac{1}{2}\left(t\,\vec{v}_1\cdot\frac{\partial}{\partial\vec{x}_1}\right)^2 + \dots\right] D(\vec{x}_1,\vec{v}_1,0) =$$

$$= D(\vec{x}_1 - \vec{v}_1 t, \vec{v}_1, 0)$$

If we consider all the particles again, we obtain

$$D(\vec{x}^N, \vec{v}^N, t) = e^{-i\hat{\Lambda}_0 t} D(\vec{x}^N, \vec{v}^N, 0) = D(\vec{x}^N - \vec{v}^N t, \vec{v}^N, 0)$$

Thus, the distribution at some time t is the same as at 0, just the positions are shifted backwards along the free-particle trajectory.

Therefore, $\exp(-i\hat{\Lambda}_0 t)$ is called the free-particle propagator.

Though note that it propagates the variables (arguments) backward in time.

1.5.4 The Resolvent

The final way to solve the initial value problem of the Liouville equation is to use the Laplace transform:

$$\tilde{D}(s) = \int_0^\infty dt\, e^{-st} D(t)$$

We need to transform the Liouville equation

$$i\frac{\partial D}{\partial t} = \hat{\Lambda} D$$

Thus

$$\int_0^\infty dt\, e^{-st}\frac{\partial D}{\partial t} = \left(e^{-st}D\right)_0^\infty - \int_0^\infty dt\,\frac{\partial}{\partial t}\left(e^{-st}\right) D = -D(0) + s\tilde{D}(s)$$

with $s > 0$.

So we have

$$i\left(-D(0) + s\tilde{D}(s)\right) = \hat{\Lambda}\tilde{D}(s)$$

$$\Rightarrow -i D(0) = (\hat{\Lambda} - is)\tilde{D}(s)$$

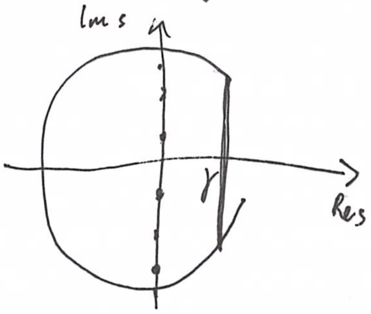
$$\Rightarrow \tilde{D}(s) = -i\underbrace{(\hat{\Lambda} - is)^{-1}}_{\hat{R}\ \leftarrow\ \text{resolvent operator}} D(0)$$

We will need the inverse Laplace transform

$$D(t) = \frac{1}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} ds\, e^{ts} \tilde{D}(s)$$

Since $\hat{\Lambda}$ has only real eigenvalues, all the singularities of $\hat{R}$ are with s being purely imaginary.

Thus, integration can be performed using the contour



Remember, that γ must be to the right of all singularities.

We also assume that operator $\hat{R}$ is bounded, thus, for any ψ with finite norm $\|\psi\|$, there is a finite constant M, such that $\|\hat{R}\psi\| < M\|\psi\|$.