Time-Dependent Thomas-Fermi Molecular Dynamics Simulations of Dense Plasmas

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Discuss an approach (i) to perform TD simulations of dense plasmas,
i.e. the real-time dynamics of partially degenerate electrons and classical ions,
using an orbital-free approximation of time-dependent density functional theory,
(ii) to access to truly dynamical processes so far inaccessible to state-of-the-art techniques

Ability to simulate dynamical processes and non-equilibrium conditions must be developed:

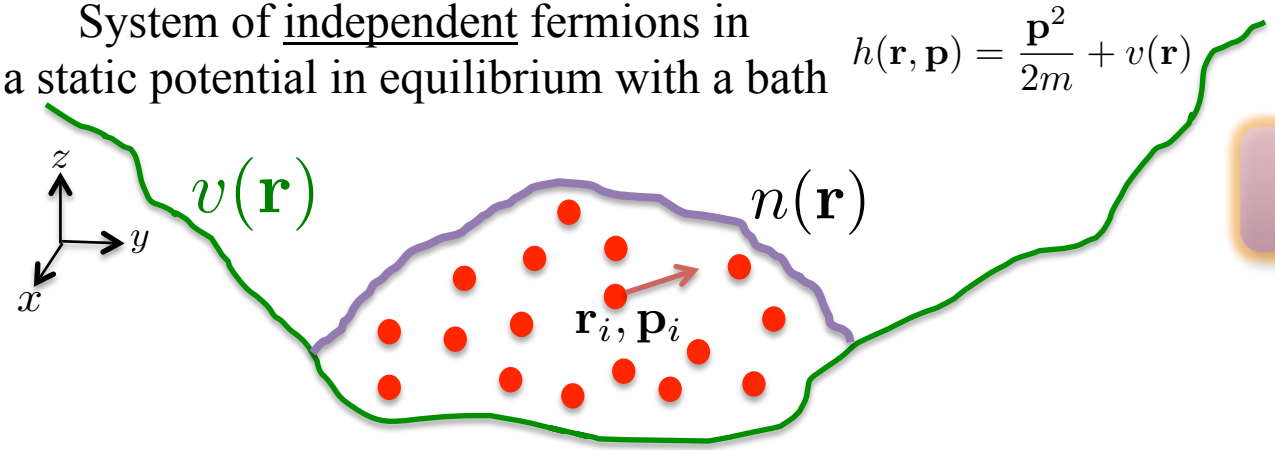
- to support basic experiments:
  - anticipated future X-ray sources will make it possible to probe genuine dynamical properties
  - measurements difficult to interpret if recorded while the diverse species are out of equilibrium
- to support application-driven experiments

This talk: - the time-dependent Thomas-Fermi model

- implementation: combination of MD and plasma physics (PIC) techniques
- preliminary results

The Thomas-Fermi approximation retains the elegance of the correct theory and provide deep physical insights.

System of independent fermions in a static potential in equilibrium with a bath $h(\mathbf{r},\mathbf{p}) = \frac{\mathbf{p}^2}{2m} + v(\mathbf{r})$



What is $n(\mathbf{r})$?

Classical : $\epsilon_{\mathbf{r},\mathbf{p}} = h(\mathbf{r},\mathbf{p})$

$$f_B(\mathbf{r},\mathbf{p}) = \frac{1}{(2\pi\hbar)^3} e^{\beta[\mu - h(\mathbf{r},\mathbf{p})]}$$

$$n(\mathbf{r}) = \int d\mathbf{p} f_B(\mathbf{r},\mathbf{p}) \propto e^{-\beta[\mu - v(\mathbf{r})]}$$

Quantum : $h(\hat{\mathbf{r}},\hat{\mathbf{p}})\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$ $\quad f_i = \frac{1}{1+e^{-\beta(\mu-\epsilon_i)}}$ (average occupation)

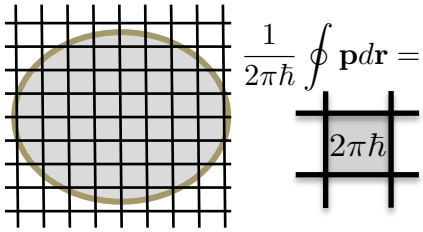
$$\hat{\rho} = 2\sum_i^{\infty} f_i |\phi_i\rangle\langle\phi_i|$$

$$n(\mathbf{r}) = \langle\mathbf{r}|\hat{\rho}|\mathbf{r}\rangle = 2\sum_{i=0}^{\infty} f_i |\phi_i(\mathbf{r})|^2$$

Probability of observing at this position a particle in state i

Thomas-Fermi approximation (1927): Old quantum mechanics: when electron is in state "i", its motion can be adequately described by means of classical mechanics

→ Large principal quantum number



$$\frac{1}{2\pi\hbar}\oint \mathbf{p}d\mathbf{r} = n = \sum_{\epsilon_i < h(\mathbf{r},\mathbf{p})} i$$

quasi/semi-classical/quantal statistical model

$\frac{d\mathbf{r}d\mathbf{p}}{(2\pi\hbar)^3}$ states per phase-space volume element *classical-like* → $f_{FD}(\mathbf{r},\mathbf{p}) = \frac{2}{(2\pi\hbar)^3}\frac{1}{1+e^{-\beta[\mu-h(\mathbf{r},\mathbf{p})]}}$ *quantal* → $n(\mathbf{r}) \approx n_{TF}(\mathbf{r}) = \int d\mathbf{p} f_{FD}(\mathbf{r},\mathbf{p})$

Originally, Thomas and Fermi considered high-Z atoms

$$v(\mathbf{r}) = -\frac{Z}{r} + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$v_H(\mathbf{r})$ = mean-field potential, a.k.a. Hartree

The calculation of atomic fields. By L. H. THOMAS, B.A., Trinity College.

[*Received* 6 November, *read* 22 November 1926.]

1. *Assumptions and the deduction from them of an equation.*

The following assumptions are made.

(1) Relativity corrections can be neglected.

(2) In the atom there is an effective field given by potential V, depending only on the distance r from the nucleus, such that

$V \to 0$ as $r \to \infty$,

$Vr \to E$, the nuclear charge, as $r \to 0$.

independent electrons in external potential

$\frac{2}{(2\pi\hbar)^3}\Theta(\mu - h(\mathbf{r},\mathbf{p}))$ (3) Electrons are distributed uniformly in the six-dimensional ase space for the motion of an electron at the rate of two for each h^3 of (six) volume. (This means one for each unit cell in the phase space of translation and rotation of a spinning electron.)

$h(\mathbf{r},\mathbf{p}) \leq 0$ The part of the phase space containing electrons is limited to that for which the orbits are closed.

$v = -Z/r + v_H$ (4) The potential V is itself determined by the nuclear charge and this distribution of electrons.

self-interaction In reality the effective field at any point depends on whether the point is empty or occupied by a foreign electron or one or another atomic electron and on the circumstances of that occupation. ?

large density These fields can only be expected to be sensibly the same or approximately calculable from the above assumptions if the density of electrons is large, that is, in the interior of heavy atoms.

Distance from nucleus
Logarithmic grid !

Cumulated number of electrons

$-X$	$3{\cdot}5 - \frac{dY}{dX}$	$\log_{10} 144 + Y$	ρ_0	Z_0	ψ_0	Z_1
0	2·150	1·1584	1·517	7·6	1·887	9·9
·1	2·015	1·0167	1·205	10·4	3·412	12·5
·2	1·880	·8614	·9572	13·7	6·008	16·0
·3	1·746	·6927	·7603	17·5	10·23	19·7
·4	1·615	·5105	·6040	21·6	16·90	24·3
·5	1·489	·3156	·4800	25·8	27·10	29·0
·6	1·371	·1086	·3811	30·1	42·26	33·4
·7	1·261	$\bar{1}$·8901	·3027	34·2	64·18	36·6
·8	1·160	$\bar{1}$·6611	·2404	38·0	95·15	39·5
·9	1·069	$\bar{1}$·4225	·1910	41·3	138·0	42·2
1·0	·987	$\bar{1}$·1752	·1517	44·2	196·1	44·7
1·1	·914	$\bar{2}$·9202	·1205	47·7	273·9	46·6
1·2	·851	$\bar{2}$·6584	·09572	48·7	376·4	47·8
1·3	·795	$\bar{2}$·3906	·07603	50·3	510·4	48·4
1·4	·747	$\bar{2}$·1176	·06040	51·5	683·8	49·3
1·5	·706	$\bar{3}$·8402	·04800	52·5	906·8	50·6
1·6	·671	$\bar{3}$·5590	·03811	53·2	1198	51·6
1·7	·642	$\bar{3}$·2746	·03027	53·8	1556	52·4
1·8	·614	$\bar{4}$·9875	·02404	54·0	2018	53·4
1·9	·595	$\bar{4}$·6979	·01910	54·4	2601	53·9
2·0	·577	$\bar{4}$·4064	·01517	54·6	3340	54·1
2·1	·564	$\bar{4}$·1134	·01205	54·8	4273	54·4
2·2	·552	$\bar{5}$·8191	·009572	54·9	5450	54·6
2·3	·542	$\bar{5}$·5238	·007603	54·9	6936	54·7
2·4	·534	$\bar{5}$·2276	·006040	55·0	8809	54·8
2·5	·527	$\bar{6}$·9306	·004800	55·0	11170	
2·6	·521	$\bar{6}$·6330	·003811	55·0	14140	
2·7	·517	$\bar{6}$·3349	·003027	55·0	17870	
2·8	·513	$\bar{6}$·0364	·002404	55·0	22580	
2·9	·510	$\bar{7}$·7376	·001910	55·0	28570	
3·0	·508	$\bar{7}$·4385	·001517	55·0	35960	

Ce (Z=55)

The values Z_1 are (unpublished) values calculated by Mr Hartree for caesium from the observed levels and which he has very kindly allowed me to include for comparison.

In conclusion, I wish to thank Professor Bohr and Professor Kramers for their encouragement when I was carrying out the numerical integration last March.

Thomas-Fermi is considered as a precursor of DFT
But DFT is essential to rigorously justify and extend Thomas-Fermi

I) Properties of an electronic system at equilibrium are completely determined by its particle density alone (Hohenberg-Kohn)

II) density of interacting particles is also the density of a fictitious, non-interacting system of particles under the influence of the Kohn-Sham (KS) potential

$$v(\mathbf{r}) = v_{KS}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$

The Time-Dependent Thomas-Fermi approximation derived following Thomas' 1926 paper

1. *Assumptions and the deduction from them of an equation.*

The following assumptions are made.

(1) Relativity corrections can be neglected.

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$V \to 0$ as $r \to \infty$,

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(3) Electrons are distributed uniformly in the six-dimensional phase space for the motion of an electron at the rate of two for each h^3 of (six) volume. (This means one for each unit cell in the phase space of translation and rotation of a spinning electron.) The part of the phase space containing electrons is limited to that for which the orbits are closed.

(4) The potential V is itself determined by the nuclear charge and this distribution of electrons.

possibly under an external TD potential $v_{ext}(\mathbf{r},t)$

$f(\mathbf{r},\mathbf{p},t)$ with *quantum statistics*

$v_H(\mathbf{r},t) = \int d\mathbf{r}' \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}$

(5) the evolution of $f(\mathbf{r},\mathbf{p},t)$ is governed by the laws of classical mechanics ⟶ Liouville equation

$$\frac{\partial f(\mathbf{r},\mathbf{p},t)}{\partial t} = \left\{ \frac{p^2}{2m} + v_{ext}(\mathbf{r},t) + v_H(\mathbf{r},t), f \right\}(\mathbf{r},\mathbf{p},t)$$

Vlasov-like equation

Semi-classical Vlasov approximation

TF can also be derived from modern quantum mechanics using a phase-space representation

Traditional representation

$$A_W(\mathbf{R},\mathbf{P}) = \int d\mathbf{x} \left\langle \mathbf{R} - \frac{\mathbf{x}}{2} | \hat{A} | \mathbf{R} + \frac{\mathbf{x}}{2} \right\rangle e^{i\mathbf{P}\cdot\mathbf{x}/\hbar}$$

$$\left\langle \mathbf{R} - \frac{\mathbf{x}}{2} \middle| \hat{A} \middle| \mathbf{R} + \frac{\mathbf{x}}{2} \right\rangle = \frac{\hbar^3}{(2\pi)^3} \int d\mathbf{P} A_W(\mathbf{R},\mathbf{P}) e^{-i\mathbf{P}\cdot\mathbf{x}/\hbar}$$

Wigner representation

$\hat{\rho}$	States	$f_W(\mathbf{R},\mathbf{P})$
$\langle A \rangle = \mathrm{Tr}\hat{\rho}\hat{A}$	Expectation values	$\langle A \rangle = \iint d\mathbf{R}d\mathbf{P} f_W(\mathbf{R},\mathbf{P}) A_W(\mathbf{R},\mathbf{P})$
$h(\hat{\mathbf{R}},\hat{\mathbf{P}}) = \frac{\hat{\mathbf{P}}^2}{2m} + v(\hat{\mathbf{R}})$	Hamiltonian	$h(\mathbf{R},\mathbf{P}) = \frac{\mathbf{P}^2}{2m} + v(\mathbf{R})$
$n(\mathbf{R}) = \langle \mathbf{R} \vert \hat{\rho} \vert \mathbf{R} \rangle$	density	$n(\mathbf{R}) = \int d\mathbf{P} f_W(\mathbf{R},\mathbf{P})$
$\hat{A}\hat{B}$	formulary	$A(\mathbf{R},\mathbf{P}) e^{\frac{\hbar}{2i}\left[\overleftarrow{\nabla}_\mathbf{R}\cdot\overrightarrow{\nabla}_\mathbf{P} - \overleftarrow{\nabla}_\mathbf{P}\cdot\overrightarrow{\nabla}_\mathbf{R}\right]} B(\mathbf{R},\mathbf{P})$

Thomas-Fermi

$$\longleftrightarrow \quad \hbar = 0$$

(explicit occurrences only !)

$$\hat{A}\hat{B} \to A(\mathbf{R},\mathbf{P})B(\mathbf{R},\mathbf{P})$$

$$\frac{1}{i\hbar}\left(\hat{A}\hat{B} - \hat{B}\hat{A}\right) \to \{A,B\}(\mathbf{R},\mathbf{P})$$

$$i\hbar\frac{d\hat{\rho}}{dt} = \left[\hat{h},\hat{\rho}\right] \longrightarrow \frac{\partial f_W}{\partial t} = \left\{h, f_W\right\}$$

TD-TF recovered

System's state: $\hat{\rho} = 2\sum_{i}^{\infty} f_i |\phi_i\rangle\langle\phi_i|$

Quantum statistics: $f(\epsilon) = \dfrac{1}{1+e^{-\beta\epsilon}}$ **Untouched** $\dfrac{\pi k_B T}{\sin(\pi k_B T s)}$

$$\rho(\mathbf{r},\mathbf{r}';\mu) = 2\sum_{i=1}^{\infty} f_i \phi_i^*(\mathbf{r}')\phi_i(\mathbf{r}) = \int_{-\infty}^{+\infty} f(\mu-\epsilon) g(\mathbf{r},\mathbf{r}';\epsilon) d\epsilon = \frac{2}{2\pi i}\int_{\alpha-i\infty}^{\alpha+i\infty} ds \tilde{f}(s)\tilde{g}(\mathbf{r},\mathbf{r}';s)e^{\mu s}$$

Spectral density: $\langle \mathbf{r}|\delta(\epsilon-\hat{h})|\mathbf{r}'\rangle = \sum_{i=1}^{\infty} \phi_i^*(\mathbf{r}')\phi_i(\mathbf{r})\delta(\epsilon-\epsilon_i)$

$\left\langle \mathbf{r}\middle| e^{-s\hat{h}} \middle|\mathbf{r}'\right\rangle$

Bloch density

Approximated

In Wigner representation $f_W(\mathbf{R},\mathbf{P}) = \dfrac{1}{2\pi i}\int_{\alpha-i\infty}^{\alpha+i\infty} ds \tilde{f}(s) g_W(\mathbf{R},\mathbf{P};s)e^{\mu s}$

$[s] = 1/\text{energy}$

$$\hat{h}e^{-s\hat{h}} = e^{-s\hat{h}}\hat{h} \iff \left[-\frac{\hbar^2}{2m}\left(\nabla^2_{\mathbf{r}} - \nabla^2_{\mathbf{r}'}\right) + \left(v(\mathbf{r}) - v(\mathbf{r}')\right)\right]\tilde{g}(\mathbf{r},\mathbf{r}';s) = 0$$

With $v(\mathbf{r}) = a_0 + a_1\mathbf{r} + a_2\mathbf{r}^2$ but no additional approximation

$$\left[-\frac{\hbar^2}{2m}\left(\nabla^2_{\mathbf{r}} - \nabla^2_{\mathbf{r}'}\right) + (\mathbf{r}-\mathbf{r}')\cdot v\left(\frac{\mathbf{r}+\mathbf{r}'}{2}\right)\right]\tilde{g}(\mathbf{r},\mathbf{r}';s) = 0$$

$\mathbf{R} = \frac{\mathbf{r}+\mathbf{r}'}{2} \quad \mathbf{x} = \mathbf{r} - \mathbf{r}'$

$$\left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{R}}\cdot\nabla_{\mathbf{x}} + \mathbf{x}\cdot\nabla_{\mathbf{R}}v(\mathbf{R})\right]\tilde{g}(\mathbf{R},\mathbf{x};s) = 0$$

Fourier with respect to x gives Wigner $g_W(\mathbf{R},\mathbf{P};s) = \int \frac{d\mathbf{x}}{(2\pi\hbar)^3}\tilde{g}(\mathbf{R},\mathbf{x};s)e^{-i\mathbf{P}\cdot\mathbf{x}/\hbar}$

$$-\frac{\mathbf{P}}{m}\cdot\nabla_R g_W + \nabla_R v(\mathbf{R})\cdot\nabla_{\mathbf{P}} g_W = 0$$

$$\{h, g_W\}(\mathbf{R},\mathbf{P}) = 0 \quad \Rightarrow \quad g_W(\mathbf{R},\mathbf{P};\mu) = \mathcal{F}\Big(h(\mathbf{R},\mathbf{P})\Big)$$

classical looking

It is tempting to assume $g_W(\mathbf{R},\mathbf{P}) = \dfrac{1}{(2\pi\hbar)^3} e^{-sh(\mathbf{R},\mathbf{P})}$ in $f_W(\mathbf{R},\mathbf{P}) = \dfrac{2}{2\pi i}\displaystyle\int_{\alpha-i\infty}^{\alpha+i\infty} ds \frac{\pi k_B T}{\sin(\pi k_B T s)} g_W(\mathbf{R},\mathbf{P};s) e^{\mu s}$

$$f_W(\mathbf{R},\mathbf{P};\mu) = \frac{2}{(2\pi\hbar)^3}\frac{1}{2\pi i}\int_{\alpha-i\infty}^{\alpha+i\infty} ds \tilde{f}(s) e^{s[\mu - h(\mathbf{R},\mathbf{P})]} = \frac{2}{(2\pi\hbar)^3}\frac{1}{1+e^{-\beta[\mu-h(\mathbf{R},\mathbf{P})]}} = f_{FD}(\mathbf{R},\mathbf{P})$$

Thomas-Fermi !!!

Comparison with exact results:

- $v(\mathbf{r}) = cste = v$

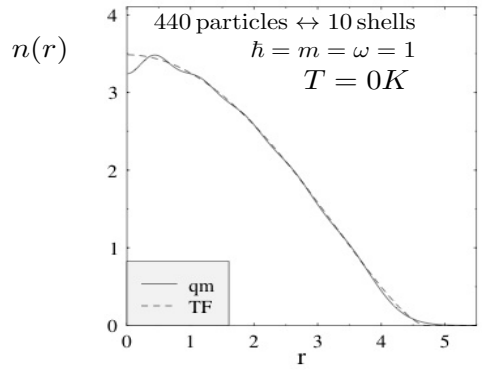
$$g_W(\mathbf{R},\mathbf{P};s) = \frac{2}{(2\pi\hbar)^3} e^{-s\left(\frac{\mathbf{P}^2}{2m}+v\right)}$$

- $v(\mathbf{r}) = \dfrac{1}{2}m\omega^2\mathbf{r}^2$

$$g_W(\mathbf{R},\mathbf{P};s) = \frac{2}{(2\pi\hbar)^3}\frac{1}{\cosh(s\hbar\omega/2)^3} e^{-s\sigma^2(s)h(\mathbf{R},\mathbf{P})} \neq \frac{2}{(2\pi\hbar)^3} e^{-sh(\mathbf{R},\mathbf{P})}$$

$$\sigma^2(s) = \frac{2}{s\hbar\omega}\tanh\left(\frac{s\hbar\omega}{2}\right) \xrightarrow{s \ll 1}$$

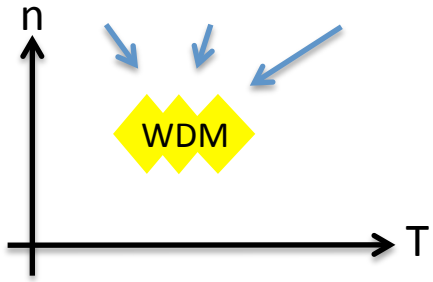
M. Brack et al. (2007)



The TF approximation is increasingly accurate when s-summation is dominated by small s contribution, namely :

- at high-temperature

or/and - at high-density



- **General potential:**

$$v\left(\mathbf{R}+\frac{\mathbf{x}}{2}\right)-v\left(\mathbf{R}-\frac{\mathbf{x}}{2}\right)=\mathbf{x}\cdot\nabla_{\mathbf{R}}v(\mathbf{R})+\ldots$$

$$\left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{R}}\cdot\nabla_{\mathbf{r}}+\left(v\left(\mathbf{R}+\frac{\mathbf{x}}{2}\right)-v\left(\mathbf{R}+\frac{\mathbf{x}}{2}\right)\right)\right]\tilde{g}(\mathbf{R},\mathbf{x};s)\approx\left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{R}}\cdot\nabla_{\mathbf{r}}+\mathbf{x}\cdot\nabla_{\mathbf{R}}v(\mathbf{R})\right]\tilde{g}(\mathbf{R},\mathbf{x};s)=0$$

Limited off-diagonal spread ?

$$\{h,g_W\}(\mathbf{R},\mathbf{P})=0$$

$$\tilde{g}(\mathbf{R},\mathbf{x};s)=2\left(\frac{2\pi m}{s}\right)^{3/2}\left(\frac{s\hbar\omega}{2\sinh(s\hbar\omega/2)}\sigma(s)\right)^3 e^{-\frac{m}{2\hbar^2 s}\frac{\mathbf{x}^2}{\sigma^2(s)}}e^{-s\sigma^2(s)v(\mathbf{R})}$$

$$\text{width}=\frac{m\omega}{2\tanh(s\hbar\omega/2)}\quad\text{increases with s}$$

$$\phi(\mathbf{r},\mathbf{r}';\mu)=2\sum_{i=1}^{\infty}f_i\phi_i^*(\mathbf{r}')\phi_i(\mathbf{r})$$

At high enough temperature, density matrix becomes highly mixed:
the underlying quantum interference and coherence effects are quenched by the incoherence introduced by the thermal average: only terms close to the diagonal survive

The static Thomas-Fermi approximation can be extended to time-dependent phenomena using time-dependent density functional theory

TDDFT: Given an initial condition, an interacting system of particles in an external, TD potential is fully characterized by its TD particle density $n(\mathbf{r},t)$

The TD density is also that of a fictitious, non-interacting system of particles in an external, time-dependent potential

$$v_{KS}(\mathbf{r},t) = v_{ext}(\mathbf{r},t) + v_H(\mathbf{r}) + v_{xc}[n](\mathbf{r},t)$$

TD Kohn-Sham equations:

$$n(\mathbf{r},t) = \sum_{j=1}^{N} |\phi_j(\mathbf{r},t)|^2$$

$$i\hbar\frac{\partial\phi_j(\mathbf{r},t)}{\partial t} = \hat{h}_{KS}(t)\phi_j(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + v_{KS}(\mathbf{r},t)\right]\phi_j(\mathbf{r},t)$$

Generalization to mixed initial states:

$$n(\mathbf{r},t) = \left\langle \mathbf{r}\middle|\hat{n}_{KS}(t)\middle|\mathbf{r}\right\rangle$$

$$i\hbar\frac{d\hat{\rho}_{KS}(t)}{dt} = \left[\hat{h}_{KS},\hat{\rho}_{KS}\right]$$

From Time-Dependent Kohn-Sham to time-dependent Thomas-Fermi

$$i\hbar\frac{\partial \rho_{KS}}{\partial t}(\mathbf{r},\mathbf{r}';t) = \left[-\frac{\hbar^2}{2m}\left(\nabla^2_{\mathbf{r}} - \nabla^2_{\mathbf{r}'}\right) + \left(v_{KS}(\mathbf{r},t) - v_{KS}(\mathbf{r}',t)\right)\right]\rho_{KS}(\mathbf{r},\mathbf{r}';t)$$

$$\rho_{KS}(t=0) = 2\sum_{j=1}^{\infty} f_j |\phi_j\rangle\langle\phi_j| \quad + \text{limited spread}$$

$$v_{KS}\left(\mathbf{R}+\frac{\mathbf{x}}{2},t\right) - v_{KS}\left(\mathbf{R}-\frac{\mathbf{x}}{2},t\right) \approx \mathbf{x}\cdot\nabla_{\mathbf{R}} v_{KS}(\mathbf{R},t)$$

$$i\hbar\frac{\partial \rho_{KS}}{\partial t}(\mathbf{R},\mathbf{x};t) = \left[-\frac{\hbar^2}{m}\nabla_{\mathbf{x}}\cdot\nabla_{\mathbf{R}} + \mathbf{x}\cdot\nabla v_{KS}(\mathbf{R},t)\right]\rho_{KS}(\mathbf{R},\mathbf{x};t)$$

Fourier transform ⟶ Wigner

$$f_W(\mathbf{R},\mathbf{P},t) = \int \frac{d\mathbf{x}}{(2\pi\hbar)^3}\rho_{KS}(\mathbf{R},\mathbf{x};t)e^{i\mathbf{P}\cdot\mathbf{x}/\hbar}$$

$$i\hbar\frac{\partial f_W}{\partial t}(\mathbf{R},\mathbf{P};t) = \left[-\frac{\hbar}{m}i\mathbf{P}\cdot\nabla_{\mathbf{R}} + i\hbar\mathbf{P}\cdot\nabla v_{KS}(\mathbf{R})\right] f_W(\mathbf{R},\mathbf{x};t)$$

$$= i\hbar\left\{\frac{\mathbf{P}^2}{2m} + v_{KS}(\mathbf{R}), f_W(\mathbf{R},\mathbf{P},t)\right\}$$

$$\frac{\partial f_W}{\partial t} = \{h_{KS}, f_W\} \qquad \int d\mathbf{P} f_W(\mathbf{R},\mathbf{P},t) = n(\mathbf{R},t)$$

Time-Dependent Thomas-Fermi

Time-Dependent Thomas-Fermi Molecular Dynamics
Simulations of Dense Plasmas

$$\frac{\partial f_W}{\partial t} = \{h_{KS}, f_W\} \qquad \int d\mathbf{P} f_W(\mathbf{R}, \mathbf{P}, t) = n(\mathbf{R}, t)$$

Despite its resemblance, this Vlasov-like equation is not the Vlasov equation of traditional plasma physics:

f_W is not the distribution function of the real electrons ; in the spirit of DFT, it provides a path to the particle density.

the mean-field potential contains an additional exchange correlation term. Computational plasma physics

f_W satisfies the requirements of the Fermi-Dirac statistics and the fermionic character Is preserved by the Vlasov dynamics: phase-space volumes are conserved.

However, the resemblance is very advantageous since it allows using numerical methods of traditional plasma physics

Time-Dependent Thomas-Fermi Molecular Dynamics of Dense Plasmas = dynamics of semi-classical (TF) electrons + classical ions

$$H_{tot}(t) = H_p + H_{ext}(t) \qquad H_p = H_i + H_e + V_{ie}$$

$$V_{ie} = \sum_{j=1}^{N_e} \sum_{J=1}^{N_i} v_{ps}(|\mathbf{r}_j - \mathbf{R}_J|)$$

In general, a similar set of equations could be used to calculate the ionic density but further simplification is achieved by treating the nuclear motion classically.

$$n_i(\mathbf{r},t) = \sum_J^{N_i} \delta(\mathbf{r} - \mathbf{R}_J(t)) + O(\mathbf{r} - \mathbf{R}_J(t))^2 \,.$$

$$M\frac{d^2\mathbf{R}_J}{dt^2} = \nabla_{\mathbf{R}_J}\left[Ze\phi_{ext}(\mathbf{R}_J,t) + \int d\mathbf{r}' n_e(\mathbf{r}',t) v_{ps}(|\mathbf{R}_J - \mathbf{r}') + \sum_{K\neq J}^{N_i} \frac{Z^2e^2}{|\mathbf{R}_J(t) - \mathbf{R}_K(t)|^2}\right]$$

Born-Oppenheimer was not used !

Our mixed quantum-classical approach can then be summarized as the self-consistent solution of Newton's equations for the ion dynamics and the Vlasov equation for the electron dynamics

$$\begin{cases} \dfrac{\partial f_W(\mathbf{r},\mathbf{p},t)}{\partial t} = \left\{ \dfrac{\mathbf{p}^2}{2m} + v_{KS}(\mathbf{r},t)\,,\ f_W(\mathbf{r},\mathbf{p},t) \right\} \\ M\dfrac{d^2\mathbf{R}_J}{dt^2} = \mathbf{F}_J(t) \end{cases}$$

The Vlasov equation is solved using the *pseudo-particle method*

The method is similar to the standard particle-in-cell (PIC), except that in traditional applications of PIC each numerical particle represents many real particles whereas here each numerical particle represents a fraction of a physical electron.

$$\frac{N_{pp}}{N_e} \sim 10^2 - 10^3 \qquad g(\mathbf{r}) = \frac{1}{(\sqrt{2\pi}\sigma)^3} e^{-\mathbf{r}^2/2\sigma^2}$$

$$f(\mathbf{r},\mathbf{p},t) \approx \frac{N_e}{N_{pp}} \sum_{i=1}^{N_{pp}} g\big(\mathbf{r}-\mathbf{r}_i(t)\big)\delta\big(\mathbf{p}-\mathbf{p}_i(t)\big)$$

with
$$\begin{cases} \dfrac{d\mathbf{r}_i}{dt} = \dfrac{\mathbf{p}_i}{m_e} \\ \dfrac{d\mathbf{p}_i}{dt} = -\displaystyle\int d\mathbf{r} g\big(\mathbf{r}-\mathbf{r}_i(t)\big)\nabla v_{KS}(\mathbf{r},t) = -\nabla_{\mathbf{r}_i} g \star v_{KS}(\mathbf{r}_i(t),t) \end{cases}$$

The dynamics is Hamiltonian
$$H_{pp} = \iint d\mathbf{r}d\mathbf{p}\Big[\frac{\mathbf{p}^2}{2m_e} + v_{KS}(\mathbf{r},t)\Big] f(\mathbf{r},\mathbf{p},t) = \sum_{i=1}^{N_{pp}} \frac{\mathbf{p}_i^{*2}}{2m_{pp}} + \sum_{i=1}^{N_{pp}} \frac{N_e}{N_{pp}} v_{KS} \star g(\mathbf{r}_i(t),t)$$

$$\begin{cases} \dfrac{d\mathbf{r}_i}{dt} = \dfrac{\mathbf{p}_i^*}{m_{pp}} \\ \dfrac{d\mathbf{p}_i^*}{dt} = -\dfrac{\partial}{\partial \mathbf{r}_i} H_{pp} = -\dfrac{N_e}{N_{pp}} \dfrac{\partial}{\partial \mathbf{r}_i} v_{KS} \star g(\mathbf{r}_i(t),t) \end{cases}$$

$$m_{pp} = \frac{N_e}{N_{pp}} m_e \quad , \quad \mathbf{p}_i^* = \frac{N_e}{N_{pp}} \mathbf{p}_i$$

The solution of the coupled electron-ion dynamics amounts to the solution of Newton's equations, which lies in the realm of classical molecular dynamics

$$\begin{cases} \dfrac{\partial f_W(\mathbf{r},\mathbf{p},t)}{\partial t} = \left\{ \dfrac{\mathbf{p}^2}{2m} + v_{KS}(\mathbf{r},t)\,,\; f_W(\mathbf{r},\mathbf{p},t) \right\} \\ M\dfrac{d^2\mathbf{R}_J}{dt^2} = \mathbf{F}_J(t) \end{cases}$$

time-dependent Thomas-Fermi

Classical molecular dynamics of N_{pp}+N_{ions} particles

$$\begin{cases} m_{pp}\dfrac{d^2\mathbf{r}_i(t)}{dt^2} = \mathbf{f}_i^{\text{ext}} + \mathbf{f}_i^{\text{ei}} + \mathbf{f}_i^{\text{H}} + \mathbf{f}_i^{\text{xc}} \\ M_I\dfrac{d^2\mathbf{R}_I(t)}{dt^2} = \mathbf{F}_I^{\text{ext}} + \mathbf{F}_I^{\text{ei}} + \mathbf{F}_I^{\text{ii}} \end{cases}$$

Remark #1: ions interact via the Coulomb interaction $\dfrac{1}{r}$ ⟹ ***particle-particle particle-mesh P³M method***

P³M which combines high-resolution of individual encounters and rapid, mesh-based, long-range force calculation

Remark #2: pseudo-particles interact via the mean field potential $v_H[n] + v_{xc}[n]$

non-local local

⟹ no direct two-body interaction

⟹ **mesh calculation: PM of P³M**

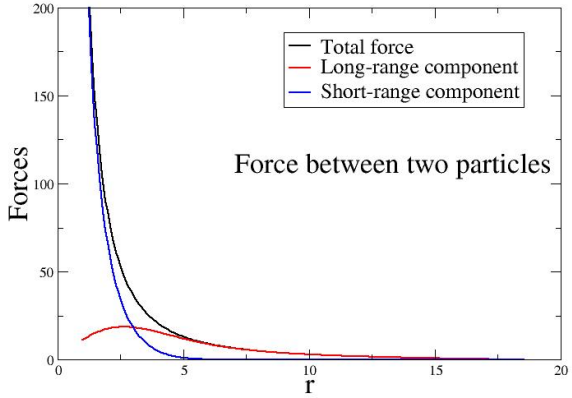
Remark #3: ions and pseudo-particles interact via a two-body potential v_{ps} and involve the same difficulties as for the ion-ion interactions

⟹ **P³M**

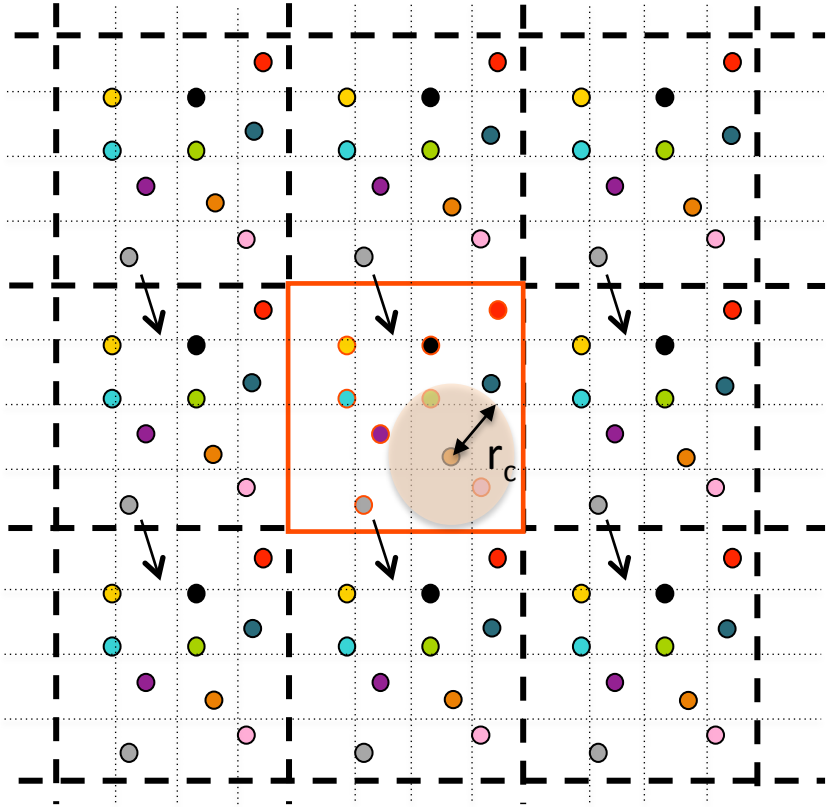
The Particle-Particle Particle-Mesh method

R.W. Hockney & J.W. Eastwood, **Computer Simulation Using Particles**
Desermo & Holm, J. Chem. Phys. (1998)
Pollock & Glosli Comp. Phys. Comm. (1996)

$$\frac{1}{r} = v_{sr}(r) + \left[\frac{1}{r} - v_{sr}(r)\right] \qquad \frac{1}{r} = \frac{\mathrm{erfc}(r/r_c)}{r} + \frac{\mathrm{erf}(r/r_c)}{r}$$



$$\mathbf{F}_I = \mathbf{F}^I_{sr} + \mathbf{F}^I_{lr}$$



Particle-Particle **PP:** $\mathbf{F}^I_{sr} = -\sum_{j\,,\,r_{IJ}<r_c} \nabla v_{sr}(r_{IJ})$

same as conventional MD
with linked neighbor lists

Particle-Mesh **PM:** $\mathbf{F}^I_{lr} = -\nabla V_{lr}(\mathbf{R}_I)$

similar to Particle-in-Cell (PIC)
although more demanding

- $\mathrm{P} \rightarrow \mathrm{M}$: assign particles on mesh
  (at least 5th order)

$$n_M(x_p) = \int_0^L dx W(x_p - x) n(x)$$

- M : solve field equation on mesh
  (e.g. Fast Fourier Transform)

$$V_{lr}(\mathbf{k}_M) = G(\mathbf{k}_M) n_M(\mathbf{k}_M)$$

- $\mathrm{M} \rightarrow \mathrm{P}$: interpolate back onto particles

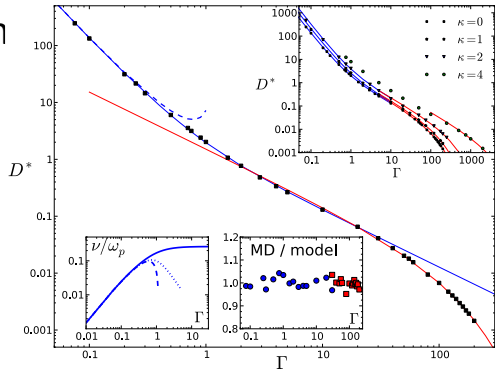
$$\mathbf{F}^I_{lr} = -q_I \sum_{\mathbf{r}_p} \nabla V_{lr}(\mathbf{r}_p) W(\mathbf{r}_I - \mathbf{r}_p)$$

Without our parallel P^{3}M code, those studies would not have been possible

Validation and extension of the Landau-Spitzer transport theories:

$$D^* = \frac{D}{a^2\omega_p} = \frac{c}{\Gamma^{5/2}} \frac{1}{\ln\left(1+\frac{d}{\Gamma^{3/2}}\right)}$$

$$D^* = \frac{D}{a^2\omega_p} = \frac{\alpha}{\Gamma} e^{-\gamma \frac{T_m}{T}}$$

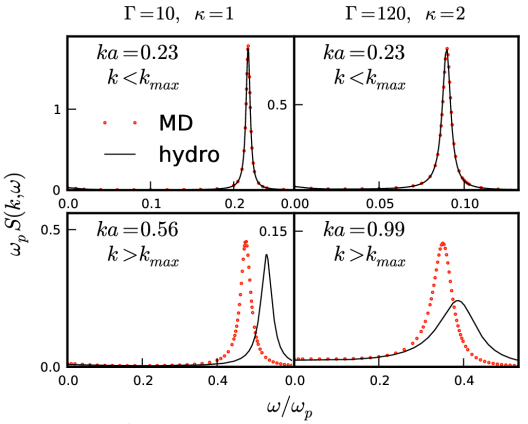


J.D., Phys. Rev. Lett. (2012)

Extend of validity of the hydrodynamic limit

$$v_{ii}(r) = e^{-r/\lambda}/r$$

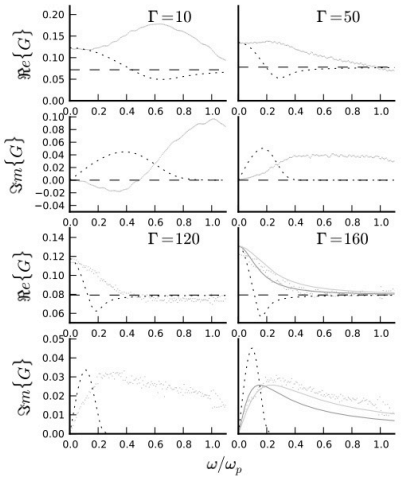
$$k < k_{max} \approx 0.43/\lambda$$



J. P. Mithen, J.D.and G. Gregori, Phys. Rev. E **83**, 015401 (2011).

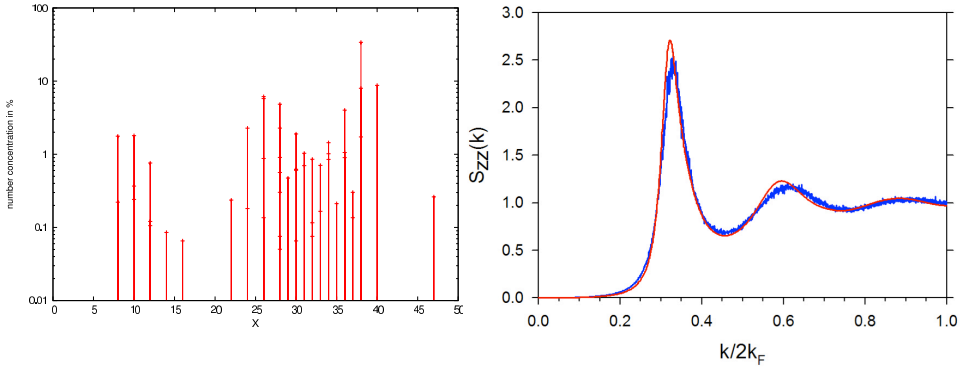
Local field corrections vs memory function to go beyond the mean-field approximation

$G(k,\omega)$

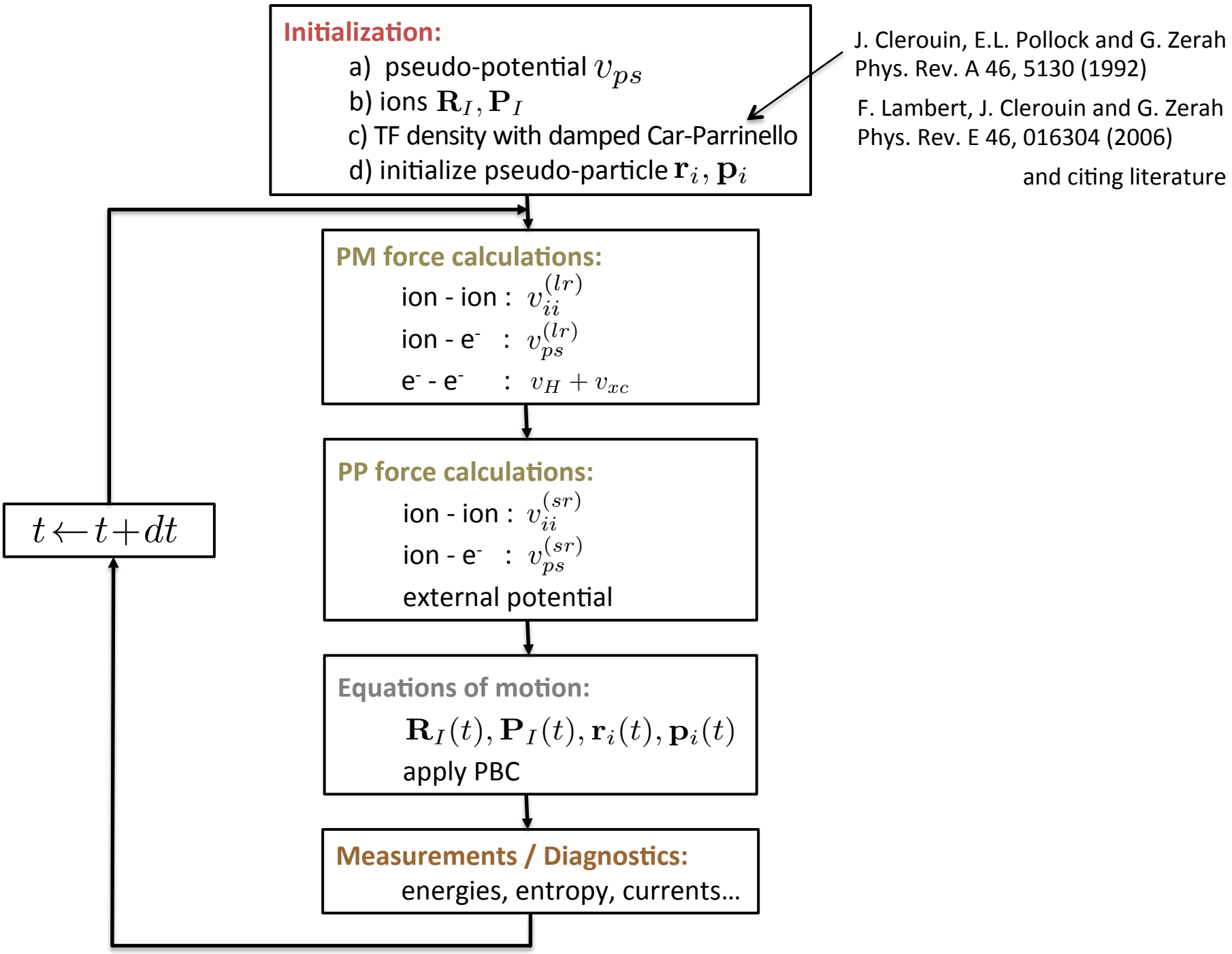


J. P. Mithen, J.D.
Phys. Rev. E 85, 056407 (2012)

Thermal conductivity of the outer crust of an accreting neutron star



J.D. , S. Gupta
ApJ. 703, 994 (2009)


Initialization:
a) pseudo-potential v_{ps}
b) ions $\mathbf{R}_I, \mathbf{P}_I$
c) TF density with damped Car-Parrinello
d) initialize pseudo-particle $\mathbf{r}_i, \mathbf{p}_i$
J. Clerouin, E.L. Pollock and G. Zerah
Phys. Rev. A 46, 5130 (1992)
F. Lambert, J. Clerouin and G. Zerah
Phys. Rev. E 46, 016304 (2006)
and citing literature
PM force calculations:
ion - ion : $v_{ii}^{(lr)}$
ion - e- : $v_{ps}^{(lr)}$
e- - e- : $v_H + v_{xc}$
PP force calculations:
ion - ion : $v_{ii}^{(sr)}$
ion - e- : $v_{ps}^{(sr)}$
external potential
Equations of motion:
$\mathbf{R}_I(t), \mathbf{P}_I(t), \mathbf{r}_i(t), \mathbf{p}_i(t)$
apply PBC
Measurements / Diagnostics:
energies, entropy, currents…
$t \leftarrow t + dt$

The numerical scheme must conserve the fermionic character

Theory

$$\frac{\partial f_W}{\partial t} = \{h_{KS}, f_W\}$$

Vlasov conserves entropy $\frac{dS(t)}{dt} = 0$

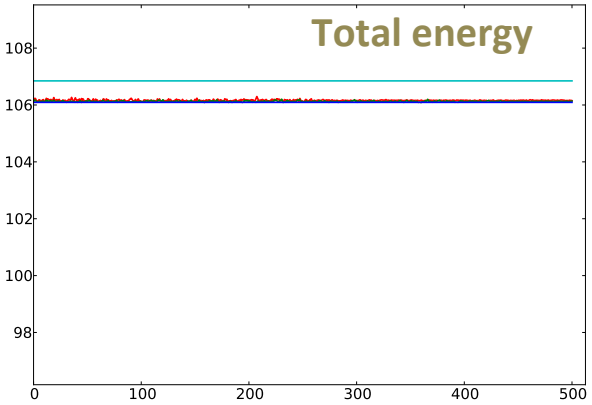
$$S(t) = -\iint d\mathbf{r}d\mathbf{p} f_W(\mathbf{r},\mathbf{p}) \ln f_W(\mathbf{r},\mathbf{p})$$

Numerical solution

$$\frac{\partial f}{\partial t} = \{h_{KS}, f\} + \mathcal{C}(f)$$

Collisions → "Boltzmannization"

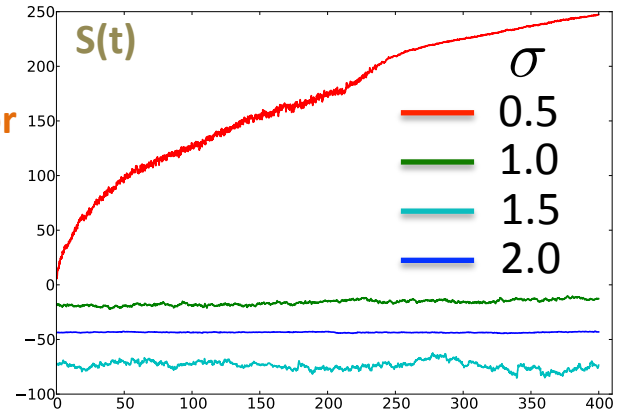
$$\frac{dS(t)}{dt} \neq 0$$



$t\omega_p$

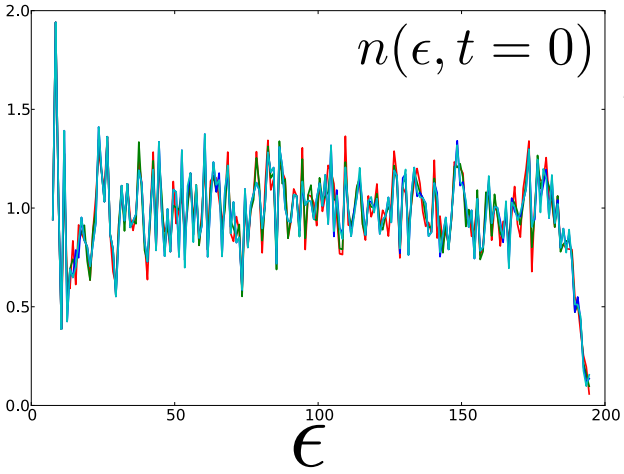
total energy conservation alone is not enough to monitor numerical stability

$$N_{pp}/N_e = 50$$



$t\omega_p$

Occupation number

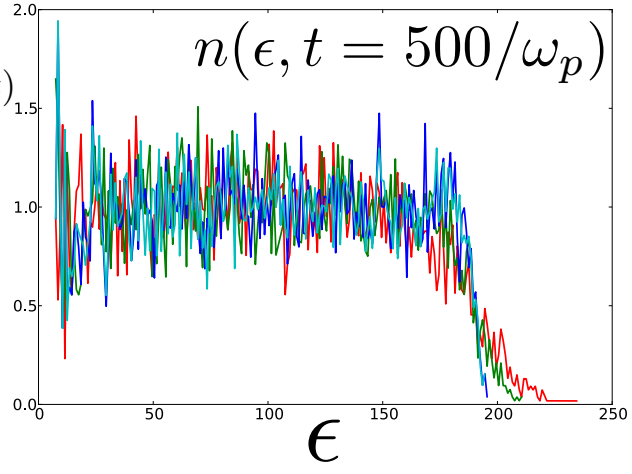


ϵ

$$S(t) = -\int d\epsilon\, g(\epsilon)\, n(\epsilon,t)\, \ln n(\epsilon,t)$$

$$n(\epsilon,t) = \frac{N_{[\epsilon,\epsilon+\Delta\epsilon]}}{N_e/N_{pp}} \frac{1}{\Delta\epsilon g(\epsilon)}$$

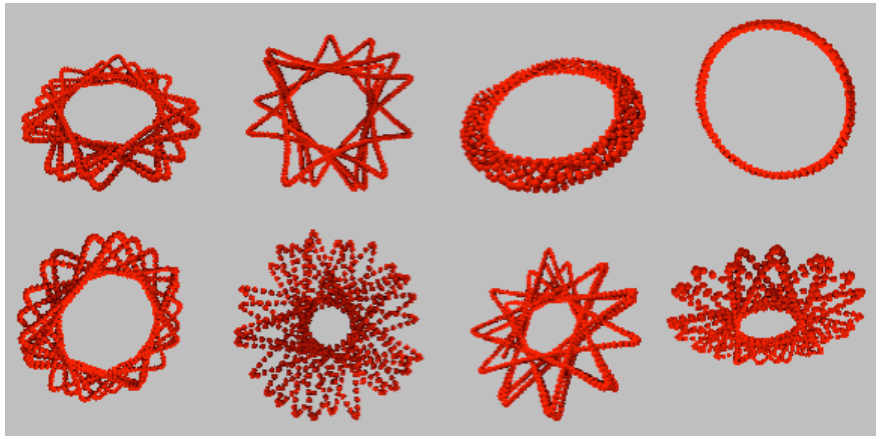
Occupation number

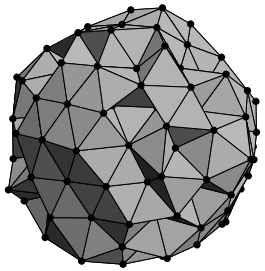


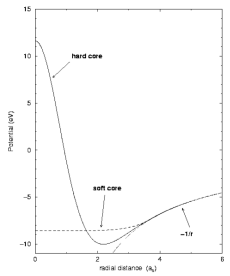
ϵ

The infinite jellium is somewhat too basic : ballistic pseudo-particle trajectories

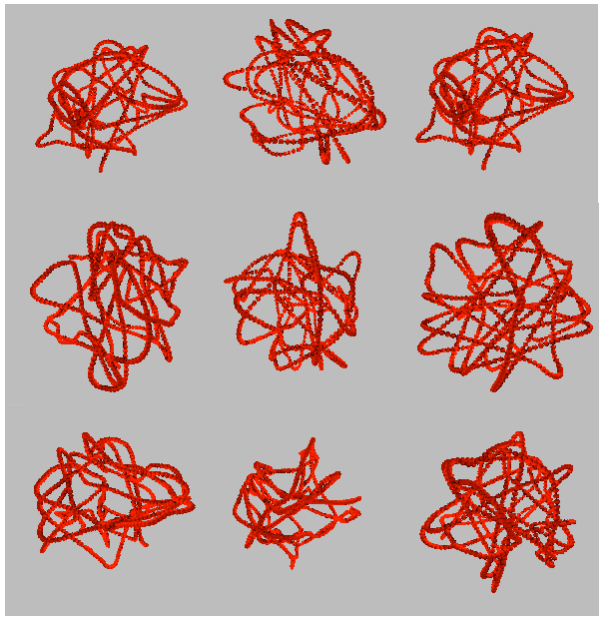
The finite jellium is richer

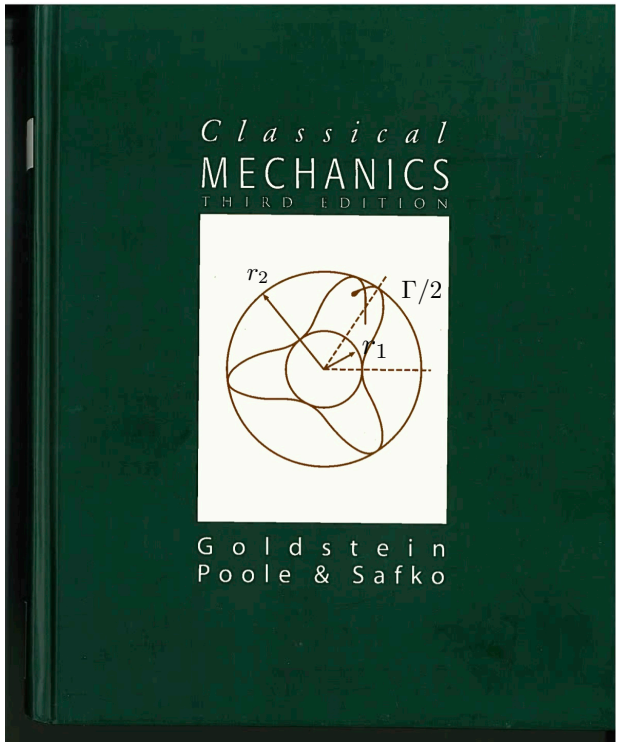






nanoplasma (metallic cluster)





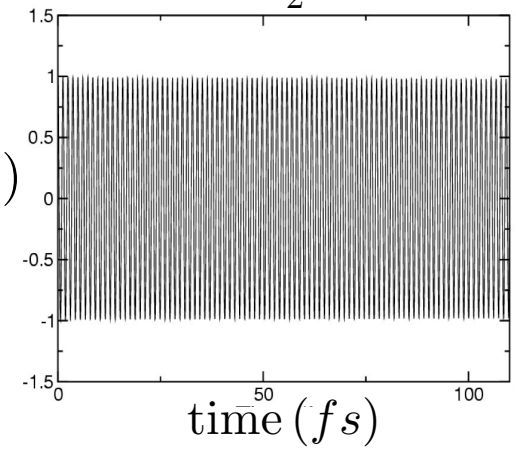
$$\omega_n(N) = n\omega_0 + N\frac{\omega_0}{2\pi/\Gamma}$$

Radial motion

precession

Electron-ion collisions and Plasmon relaxation

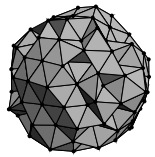
$$v_{ext}(\mathbf{r}) = \frac{1}{2} m\omega^2 r^2$$

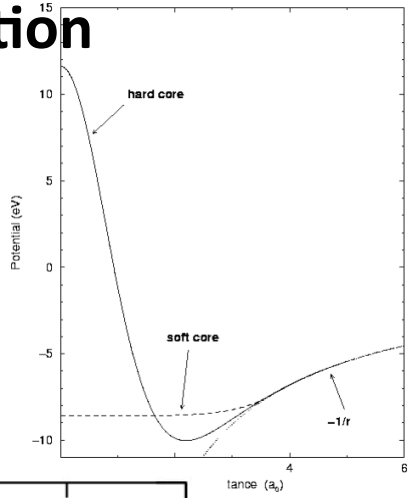


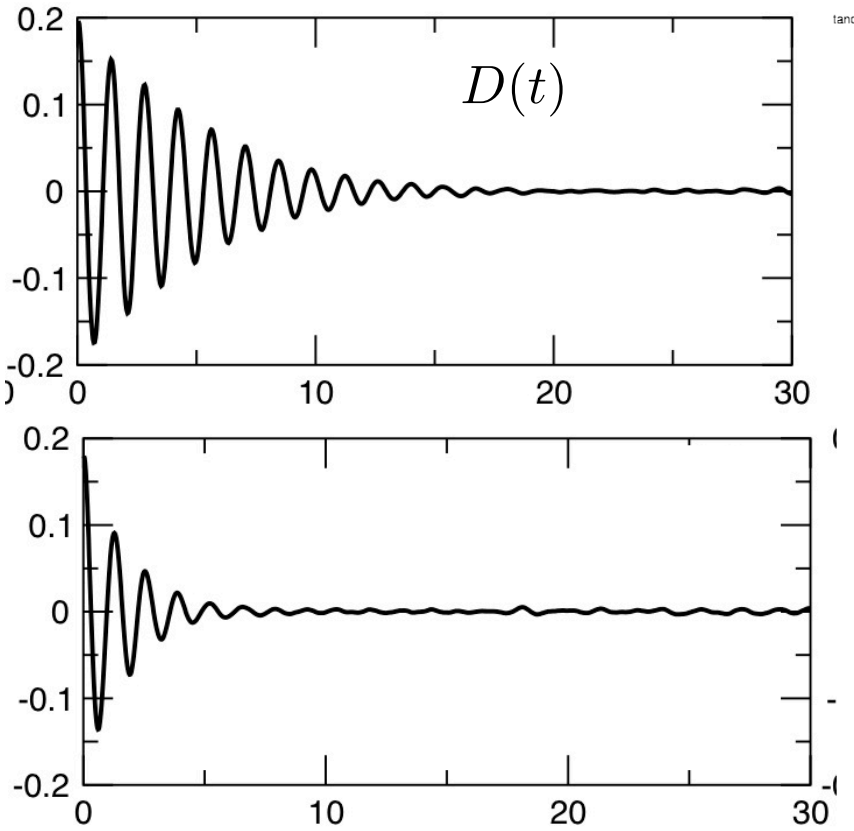
$$n(\mathbf{r},t) = n_0\big(\mathbf{r} + e\mathbf{D}(t)\big)$$

Harmonic potential theorem

$$v_{ext}(\mathbf{r}) = \sum_{I=1}^{N=196} v_{ps}(||\mathbf{r} - \mathbf{R}_I|$$







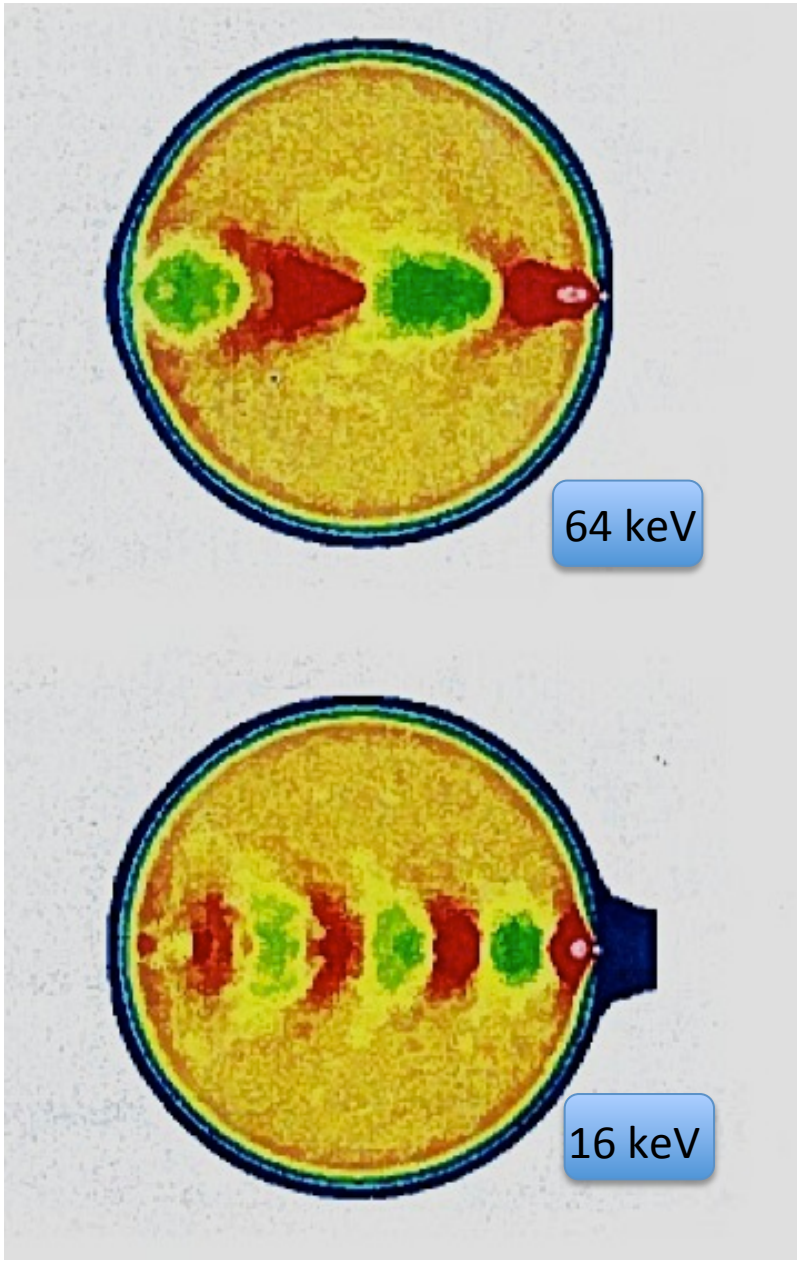
$$\mathbf{D}(t) \approx \mathbf{D}_0 e^{-\gamma t/2}\cos(\omega_\gamma t)$$

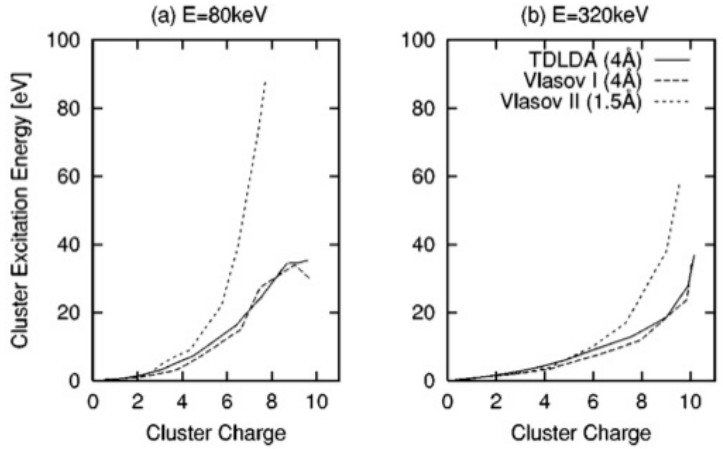
$$\omega_\gamma^2 = \omega^2 - \gamma^2/4$$

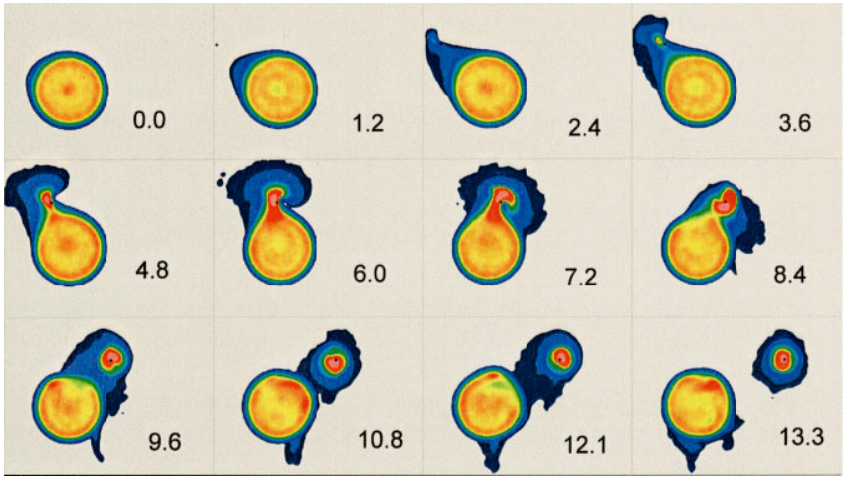
relaxation time $\tau = \dfrac{2\hbar}{\gamma}$

We hope to perform similar calculation of the electrical conductivity

Stopping power calculation







L. Plagne , C. Guet (2000)

Conclusion :

Discuss an approach to perform TD simulations of dense plasmas
using an orbital-free approximation of time-dependent density functional theory

Challenge: xc potentials beyond local density and time approximation ?

Looking for a postdoc position ?
Please come talk to me or contact me at
daligaul@lanl.gov .