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ModeCouplingTheory.jl: A solver for mode-coupling-theory-like integro-differential equations

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Software

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Summary

The mode-coupling theory of the glass transition is one of the most successful theories for predicting the dynamics of dense liquids to date. In the regime where it is applicable, the theory gives a set of detailed numerical and analytical predictions for the structural relaxation dynamics upon supercooling. In particular, the theory provides closed equations for dynamic correlation functions of the microscopic density field, including observables such as the coherent and incoherent intermediate scattering functions and the mean-squared displacement. These mode-coupling theory equations take the form of an integro-differential equation, i.e., a generalized Langevin equation, the kernel of which represents the coupling between different "relaxation modes". Because these equations are difficult to solve numerically due to their non-linearity and the long-livedness of the solutions, specialized algorithms have been developed to tackle this issue. `ModeCouplingTheory.jl` is a package that implements such an algorithm, including a number of convenient features that make it simple to solve the complex equations involved even for those not well-versed in the theoretical and numerical background traditionally required.

Statement of need

The mode-coupling theory of the glass transition (MCT) is at the forefront of the study of the glass transition (Ulf Bengtzelius et al., 1984; Das, 2004; Götze, 2009; Janssen, 2018; Leutheusser, 1984; Reichman & Charbonneau, 2005) and has been applied to an abundance of different systems and scenarios in the past forty years. See for example versions of MCT including multiple particle species (Franosch & Voigtmann, 2002; Götze & Voigtmann, 2003; Luo et al., 2022; Weysser et al., 2010), confinement (Krakoviack, 2007; Lang et al., 2010), self-propelling particles (Berthier & Kurchan, 2013; Debets & Janssen, 2023; Feng & Hou, 2017; Liluashvili et al., 2017; Reichert et al., 2021; Szamel, 2016), high dimensionalities (Ikeda & Miyazaki, 2010; Schmid & Schilling, 2010), and molecular particles (Chong et al., 2000; Chong & Hirata, 1998; Schilling & Scheidsteger, 1997; Theis et al., 2000; Winkler et al., 2000) to name a few. Before the conception of the software this paper is based on, there was no open-source integrator for MCT-like equations available. This meant that each time an improvement, extension or application to the theory was employed, a new in-house integrator needed to be developed or adapted. `ModeCouplingTheory.jl` aims at providing an open-source and tested implementation of the scheme introduced by Fuchs et al. (1991), that is performant and easy to extend to new systems, yet simple to call interactively from dynamic languages

such as Python. As of writing, it has been used for several scientific works (Kerr Winter et al., 2023; Laudicina et al., 2022, 2023; Pihlajamaa et al., 2023).

The main equation that this package aims to solve is of the form

$$\alpha\ddot{F}(t) + \beta\dot{F}(t) + \gamma F(t) + \delta + \int_0^t d\tau K(t-\tau)\dot{F}(\tau) = 0$$

in which α, β, γ, and δ are coefficients (possibly dependent on time), $K(t) = K(F(t), t)$ is the memory kernel, and $F(t)$ is the function that is being solved for. Memory kernels for solving the most commonly encountered models, such as standard (multi-component) MCT, including tagged-particle correlators, and mean squared displacements, are implemented, and it is straightforward to implement custom memory kernels. Internally, the software completely separates the memory kernel, the type of equation, and the solver, each of which can be independenty extended by a user.

The documentation details the features of this software, which among others include

1. Generality: the code was developed with generality in mind. For example, the code works for types between which product operation is defined among α, β, γ, K on the left and F on the right, returning something of the same type as F and δ. This implies that the code works for functions F that are scalar valued (schematic models), as well as those that are vectors of floating point numbers (standard MCT), and vectors with elements of different types. The latter could include, for example, numbers with measurement errors, dual numbers, and immutable matrices.
2. Extensibility: the solvers are easily extended to deal with coupled sets of equations that arive, e.g., in extensions of MCT to describe tagged-particle dynamics, or in certain asymptotic models.
3. Speed: the code is developed for performance. The solver allocates little memory and uses BLAS implementations for linear algebra where applicable (Lawson et al., 1979). The memory kernels of the single component and multi-component MCT as well as their tagged variants are implemented using Bengtzelius' trick, yielding algorithmic speed-up compared to more naive implementations (U. Bengtzelius, 1986).
4. Ease of use: solving the equations of standard MCT takes very few lines of code, see the example below. While written in Julia, the code can straightforwardly be called from Python and other languages.
5. Measurement errors: by leveraging the generality of the software it is straightforward to do standard error propagation through the solver.
6. Non-ergodicity parameters: there is built-in functionality for finding the long-time limits of the solution of the MCT equations.

Example Use

To solve the standard MCT equations in three dimensions for hard spheres using the Percus-Yevick structure factor (Wertheim, 1963), one may run the following code. See the documentation for a more in-depth explanation.

```
using ModeCouplingTheory
# the wave vector grid
Nk = 100; kmax = 40.0; dk = kmax/Nk; k = range(dk/2, kmax-dk/2, length=Nk)

# physical parameters
kBT = 1.0; m = 1.0; ρ = 0.983
```

```julia
# Hard-Sphere Percus-Yevick structure factor for this density
A = 5688.95; B = 2183.01; C = 661.463; D = 66.0759; E = 314.311;
Sk = @. k^6 /
  (A + B*k^2 + k^6 - (A - C*k^2 + D*k^4)*cos(k) - (A + E*k^2)*k*sin(k))

# initial conditions and coefficients
F0 = Sk; ∂F0 = zeros(Nk)
α = 0.0; β = 1.0; γ = @. k^2*kBT/(m*Sk); δ = 0.0

# construct the equation and solve it
kernel = ModeCouplingKernel(ρ, kBT, m, k, Sk)
equation = MemoryEquation(α, β, γ, δ, F0, ∂F0, kernel)
sol = solve(equation)

# plot the solution for several values of k
using Plots
p = plot(xlabel="log10(t)", ylabel="F(k,t)/S(k)",
         ylims=(0,1), xlims=(-6, 6))
for ik = [7, 18, 25, 39]
    t = get_t(sol)
    Fk = get_F(sol, :, ik)
    plot!(p, log10.(t), Fk/Sk[ik], label="k = $(k[ik])", lw=3)
end
display(p)
```

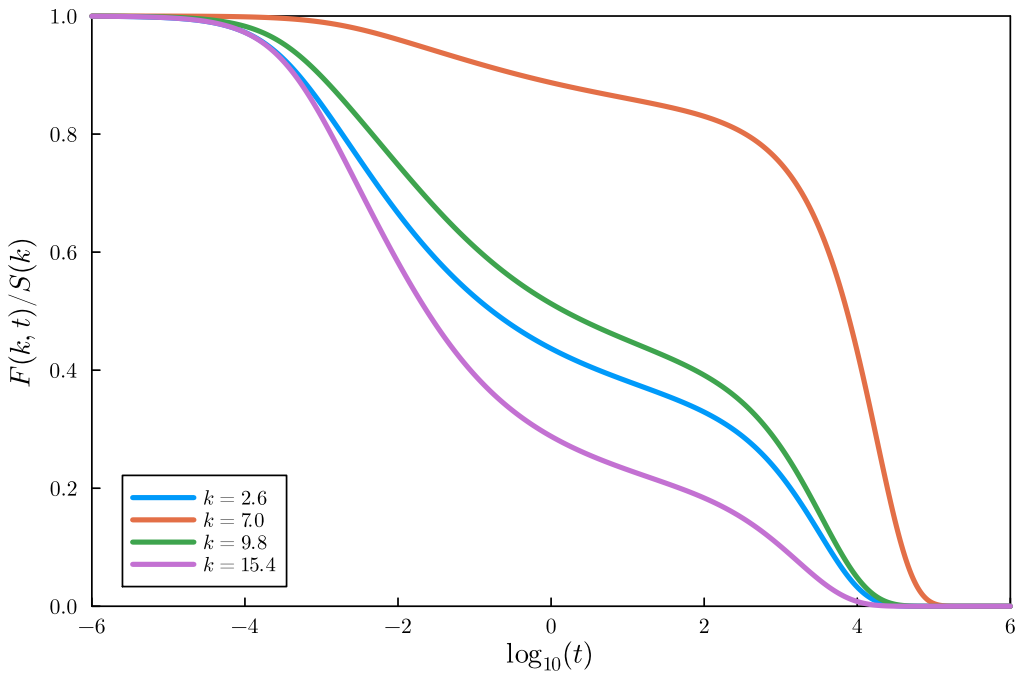

Figure 1: The code above yields this figure, which shows the intermediate scattering function, obtained with MCT, as a function of time for different values of k.

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References

Bengtzelius, U. (1986). Dynamics of a Lennard-Jones system close to the glass transition. *Phys. Rev. A*, *34*(6), 5059. https://doi.org/10.1103/PhysRevA.34.5059

Bengtzelius, Ulf, Götze, W., & Sjolander, A. (1984). Dynamics of supercooled liquids and the glass transition. *J. Phys. C: Solid State Phys.*, *17*(33), 5915. https://doi.org/10.1088/0022-3719/17/33/005

Berthier, L., & Kurchan, J. (2013). Non-equilibrium glass transitions in driven and active matter. *Nat. Phys.*, *9*(5), 310–314. https://doi.org/10.1038/nphys2592

Chong, S.-H., Götze, W., & Singh, A. P. (2000). Mode-coupling theory for the glassy dynamics of a diatomic probe molecule immersed in a simple liquid. *Phys. Rev. E*, *63*(1), 011206. https://doi.org/10.1103/physreve.63.011206

Chong, S.-H., & Hirata, F. (1998). Mode-coupling theory for molecular liquids based on the interaction-site model. *Phys. Rev. E*, *58*(5), 6188. https://doi.org/10.1063/1.58544

Das, S. P. (2004). Mode-coupling theory and the glass transition in supercooled liquids. *Rev. Mod. Phys.*, *76*(3), 785. https://doi.org/10.1103/revmodphys.76.785

Debets, V. E., & Janssen, L. M. C. (2023). Mode-coupling theory for mixtures of athermal self-propelled particles. *J. Chem. Phys.*, *159*, 014502. https://doi.org/10.1063/5.0155142

Feng, M., & Hou, Z. (2017). Mode coupling theory for nonequilibrium glassy dynamics of thermal self-propelled particles. *Soft Matt.*, *13*(25), 4464–4481. https://doi.org/10.1039/c7sm00852j

Franosch, T., & Voigtmann, T. (2002). Completely monotone solutions of the mode-coupling theory for mixtures. *J. Stat. Phys.*, *109*, 237–259. https://doi.org/10.1023/A:1019991729106

Fuchs, M., Götze, W., Hofacker, I., & Latz, A. (1991). Comments on the alpha-peak shapes for relaxation in supercooled liquids. *J. Phys.: Condens. Matt.*, *3*(26), 5047. https://doi.org/10.1088/0953-8984/3/26/022

Götze, W. (2009). *Complex dynamics of glass-forming liquids: A mode-coupling theory* (Vol. 143). Oxford University Press on Demand. https://doi.org/10.1093/acprof:oso/9780199235346.001.0001

Götze, W., & Voigtmann, T. (2003). Effect of composition changes on the structural relaxation of a binary mixture. *Phys. Rev. E*, *67*(2), 021502. https://doi.org/10.1103/PhysRevE.67.021502

Ikeda, A., & Miyazaki, K. (2010). Mode-coupling theory as a mean-field description of the glass transition. *Phys. Rev. Lett.*, *104*(25), 255704. https://doi.org/10.1103/PhysRevLett.104.255704

Janssen, L. M. C. (2018). Mode-coupling theory of the glass transition: A primer. *Front. Phys.*, *6*, 97. https://doi.org/10.3389/fphy.2018.00097

Kerr Winter, M., Pihlajamaa, I., Debets, V. E., & Janssen, L. M. C. (2023). A deep learning approach to the measurement of long-lived memory kernels from generalized Langevin dynamics. *J. Chem. Phys.*, *158*(24). https://doi.org/10.1063/5.0149764

Krakoviack, V. (2007). Mode-coupling theory for the slow collective dynamics of fluids adsorbed in disordered porous media. *Phys. Rev. E*, *75*(3), 031503. https://doi.org/10.1103/PhysRevE.75.031503

Lang, S., Boţan, V., Oettel, M., Hajnal, D., Franosch, T., & Schilling, R. (2010). Glass transition in confined geometry. *Phys. Rev. Lett.*, *105*(12), 125701. https://doi.org/10.1103/PhysRevLett.105.125701

Laudicina, C. C. L., Luo, C., Miyazaki, K., & Janssen, L. M. C. (2022). Dynamical susceptibilities near ideal glass transitions. *Phys. Rev. E*, *106*(6), 064136. https://doi.org/10.1103/PhysRevE.106.064136

Laudicina, C. C. L., Pihlajamaa, I., & Janssen, L. M. C. (2023). Competing relaxation channels in continuously polydisperse fluids: A mode-coupling study. *arXiv Preprint arXiv:2306.03992*. https://doi.org/10.48550/arXiv.2306.03992

Lawson, C. L., Hanson, R. J., Kincaid, D. R., & Krogh, F. T. (1979). Basic linear algebra subprograms for Fortran usage. *ACM Trans. Math. Softw.*, *5*(3), 308–323. https://doi.org/10.1145/355841.355847

Leutheusser, E. (1984). Dynamical model of the liquid-glass transition. *Phys. Rev. A*, *29*(5), 2765. https://doi.org/10.1103/PhysRevA.29.2765

Liluashvili, A., Ónody, J., & Voigtmann, T. (2017). Mode-coupling theory for active Brownian particles. *Phys. Rev. E*, *96*(6), 062608. https://doi.org/10.1103/PhysRevE.96.062608

Luo, C., Robinson, J. F., Pihlajamaa, I., Debets, V. E., Royall, C. P., & Janssen, L. M. C. (2022). Many-body correlations are non-negligible in both fragile and strong glassformers. *Phys. Rev. Lett.*, *129*(14), 145501. https://doi.org/10.1103/PhysRevLett.129.145501

Pihlajamaa, I., Debets, V. E., Laudicina, C. C. L., & Janssen, L. M. C. (2023). Unveiling the anatomy of mode-coupling theory. *arXiv Preprint arXiv:2307.03443*. https://doi.org/10.48550/arXiv.2307.03443

Reichert, J., Mandal, S., & Voigtmann, T. (2021). Mode-coupling theory for tagged-particle motion of active Brownian particles. *Phys. Rev. E*, *104*(4), 044608. https://doi.org/10.1103/PhysRevE.104.044608

Reichman, D. R., & Charbonneau, P. (2005). Mode-coupling theory. *J. Stat. Mech. Theory Exp.*, *2005*(05), P05013. https://doi.org/10.1088/1742-5468/2005/05/P05013

Schilling, R., & Scheidsteger, T. (1997). Mode coupling approach to the ideal glass transition of molecular liquids: Linear molecules. *Phys. Rev. E*, *56*(3), 2932. https://doi.org/10.1103/PhysRevE.56.2932

Schmid, B., & Schilling, R. (2010). Glass transition of hard spheres in high dimensions. *Phys. Rev. E*, *81*(4), 041502. https://doi.org/10.1103/PhysRevE.81.041502

Szamel, G. (2016). Theory for the dynamics of dense systems of athermal self-propelled particles. *Phys. Rev. E*, *93*(1), 012603. https://doi.org/10.1103/PhysRevE.93.012603

Theis, C., Sciortino, F., Latz, A., Schilling, R., & Tartaglia, P. (2000). Test of molecular mode coupling theory for general rigid molecules. *Phys. Rev. E*, *62*(2), 1856. https://doi.org/10.1103/PhysRevE.62.1856

Wertheim, M. (1963). Exact solution of the Percus-Yevick integral equation for hard spheres. *Phys. Rev. Lett.*, *10*(8), 321. https://doi.org/10.1103/PhysRevLett.10.321

Weysser, F., Puertas, A. M., Fuchs, M., & Voigtmann, T. (2010). Structural relaxation of polydisperse hard spheres: Comparison of the mode-coupling theory to a Langevin dynamics simulation. *Phys. Rev. E*, *82*(1), 011504. https://doi.org/10.1103/PhysRevE.82.011504

Winkler, A., Latz, A., Schilling, R., & Theis, C. (2000). Molecular mode-coupling theory applied to a liquid of diatomic molecules. *Phys. Rev. E*, *62*(6), 8004. https://doi.org/10.1103/PhysRevE.62.8004