Thermal Conductivity calculation using a Green-Kubo method

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Introduction

Over the past few decades, technologies have been progressed towards designing and manufacturing micro and nanometer scale electro-mechanical devices (Moore & Shi, 2014). In order to properly operate those micro or nanoscale devices, the thermal management should be treated carefully as insignificant phenomena at large scale would become dominant at small scales. The examples where thermal transport is important are LED technology, thermoelectric, Gas adsorption systems (e.g. Metal-Organic Frameworks), and Nanometer scale transistors (e.g. NanoFETs). In al those applications, there is a need to design materials with tailored thermal properties for the applications of need. For that, the thermal conductivity of materials needs to be calculated using atomistic simulations. It would help us to understand the heat transport mechanism at atomic level, which gives an insight that can not be obtained in an experiment and allow us to study the structure-property relationships. The objective of the paper is to calculate the thermal conductivity of Lennard-jones liquid Argon using the equilibrium Green – Kubo method.

Summary of two papers:

Paper 1: Thermal conductivity decomposition and analysis using molecular dynamics simulations. Part I. Lennard-Jones argon (McGaughey & Kaviany, 2004).

It is important to mention that an inspiration for this project comes mainly from this paper and we aim to reproduce the thermal conductivity results. Thus, this paper is summarized rigorously than the other paper.

The authors start the paper with discussing techniques other than the classical Molecular Dynamics (MD) simulation to predict the thermal conductivity, which are the application of Boltzmann transport equation under the relaxation time approximation (Ziman, 2007) and the method proposed by Cahill and Pohl (CP) (Cahill & Pohl, 1989). According to the paper, multiple simplifications and conjectures are needed to obtain the solvable forms of these techniques. Furthermore, it can be hard to connect the thermal transport properties to atomic structure of materials that do not allow to study the structure-property relationships. Contrary, in MD simulations, no assumptions are needed prior calculating the thermal conductivity. Only an atomic structure and suitable force fields (interatomic potentials) to describe the physics of interparticle interaction are required. Latter can be obtained using an ab initio electronic structure calculation or fitting to experimental data. The paper uses molecular dynamics simulation and equilibrium Green-Kubo formula to calculate the thermal conductivity of Lennard- Jones (LJ) argon in FCC crystal, amorphous and liquid phases. It is assumed that the electronic effects are implicitly included in force fields, which is an appropriate assumption for argon that have filled electron shells. All necessary data to compute thermal conductivity are collected in micro-canonical NVE (constant mass, volume and energy) ensemble at zero pressure. The timestep used is 4.285 fs, which is equal to 0.002 in dimensionless LJ units, which was found to be enough to capture the

vibrational motion of atoms. Cubic simulation box with 256 atoms and periodic boundary conditions in all directions are used in simulations. Three temperatures of 80, 90 and 100K for the liquid argon phase are considered in the paper. The experimentally determined melting temperature of argon is 83.8 K; however, in MD simulation, the melting temperature is not well defined. Authors used NpT (constant mass, pressure and temperature) ensemble to calculate the density that gives zero pressure. A Nose-Hoover thermostat and a Berendsen barostat are used to control the temperature and pressure, respectively. Authors averaged five different simulations with different initial velocity distributions to have phase space well explored.

Paper 2: Thermal conductivity of solid argon from molecular dynamics simulation (Tretiakov & Scandolo, 2004).

This paper also uses equilibrium Green-Kubo technique to calculate the thermal conductivity of Lennard–Jones solid argon at high temperature regime. At high temperatures, interatomic interactions can be assumed as purely classical and quantum effects are considered to be negligible. The simulations run at zero pressure and at temperatures between 10 and 75 K. Important takeaway from the paper is that the discrepancy in thermal conductivity results for solid argon were less than 20% of experimentally found values, which indicated that the Green-Kubo method is valid to be used in predicting the transport properties (e.g. thermal conductivity). The temperatures were controlled using Nose-Hoover thermostat and the dimensionless LJ timestep used was 0.002. Cut-off radius of 2.5σ was used in LJ pair potential. Cubic simulation box with 108 atoms was used in the simulations, which were sufficient to eliminate the size effects. Although the paper is about solid argon, some simulation details such as cut-off radius, timestep, total number of timestep gives guidelines on how to run the simulations properly. Additionally, they provided a discretized version of Green-Kubo formula, which is used in this paper.

Theory

Heat conduction is the transport of thermal energy from hotter region to colder region of a body that leads to thermal equilibrium (Bird et al., 2007). The fundamental law of thermal conduction is the *Fourier's law of heat conduction* that is given by:

$$\boldsymbol{q} = -\boldsymbol{\kappa}\nabla T$$

where, $\boldsymbol{q}$ is a heat flux (W/m2), $\boldsymbol{\kappa}$ is a thermal conductivity (W/m-K), and ∇T is a temperature gradient (K/m). Fourier's law states that the heat flux is proportional to the temperature gradient where the constant of proportionality is known as thermal conductivity, κ. The thermal conductivity depends on the temperature and the density of a system. Calculation of the thermal conductivity is not straightforward, and it is hard to calculate it from first principles calculation. There are two main MD methods for thermal conductivity calculation: non-equilibrium molecular dynamics method (NEMD) and equilibrium molecular dynamics method (EMD). In NEMD

method, also known as direct method, temperature gradient is applied, and heat flux is measured, or vice versa. Typical direct methods are direct thermostatting method (Ikeshoji & Hafskjold, 1994), reverse perturbation of Muller-Plathe, and aggregate variant of Muller-Plathe method (Müller-Plathe, 1997). Illustration of direct thermostatting method can be seen in the figure1, where two thermostatted regions (one hot and one cold) are applied at both ends of simulation box. The kinetic energy subtracted from the cold region should be equal to the kinetic energy added to the hot region. In Muller-Plathe method, the velocity of coldest particle with minimum kinetic energy in the hot region is exchanged with the velocity of hottest atom in the cold region, which leads to transfer of kinetic energy.

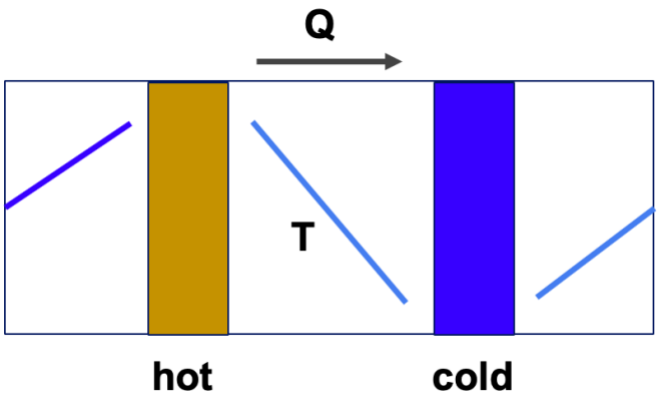

Figure 1. Illustration of direct thermostatting method.

The Green-Kubo method is based on the linear response theorem, where the response of the system to equilibrium fluctuations is analyzed. Then, thermal conductivity of system is related to the time integral of heat current – the heat flux auto-correlation function (HFACF). For an isotopic system, the Green – Kubo formula is given by:

$$k = \frac{1}{3k_b V T^2} \int_0^\infty \langle \boldsymbol{q}(t)\boldsymbol{q}(0)\rangle dt$$

(MacQuarrie, 1976)

where $\langle \boldsymbol{q}(t)\boldsymbol{q}(0)\rangle$ – heat flux autocorrelation function (HCACF), which denotes the strength of correlation between heat currents at time zero and time t, V is volume and T is temperature. The angle bracket means ensemble average. In MD simulation, it is assumed that the system behaves ergodically where the ensemble average is equal to the time average. Typically, the fluctuations would be high at the beginning of correlation time, but decays quickly. One needs to make sure that the HCACF reaches zero before the maximum correlation length. Thermal conductivity converges when HCACF reaches the point where it fluctuates around zero. The microscopic heat flux is given by:

$$\boldsymbol{q} = \sum_i E_i \boldsymbol{v_i} + \frac{1}{2}\sum_{i,j} (\boldsymbol{F_{ij}} \cdot \boldsymbol{v_i}) \boldsymbol{r_{ij}}$$

(MacQuarrie, 1976)

where E_i is the kinetic and potential energies of particle i, and $\boldsymbol{v_i}$ is the velocity vector of particle i. $\boldsymbol{F_{ij}}$ and $\boldsymbol{r_{ij}}$ are interparticle force vector and separation vector between particles i and j, respectively. It can be difficult to get a converged value of thermal conductivity using the Green-Kubo method, and it might require huge computational resources. As opposed to running a single simulation, it is possible to average the HCACF results of several independent shorter simulations prior calculating the thermal conductivity, which ensures the sufficient sampling of phase space.

Simulation Procedures

To maintain simplicity for all simulations throughout this project, Argon is chosen as the material of study which is described with a very good accuracy by a simple Lennard-Jones (LJ) interatomic pair potential. This potential ($\phi(r_{ij})$) is described as,

$$\phi(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

Where r_{ij} is the distance between atoms *i* and *j*. For argon, the values of the parameters ϵ and σ are 1.67×10^{-21}J and 3.40×10^{-10} m, respectively. Because of the LJ potential being so simple to use, it makes calculations are modifications to the code easier and faster. For calculation purposes, 256 liquid Argon is considered. This is achieved by varying the operating temperature of the system.

Before implementing the Green-Kubo algorithm to calculate the HCACF and the thermal conductivity, we would have to generate heat flux data. The flow of the simulation is shown in **Figure 2**. At first, each simulation is made sure that the pressure is near 0 MPa which can be achieved by interpolating the simulation box length with the pressure outputted for that temperature. The ideal method to reach zero pressure would be to perform an *NpT* simulation before turning the system into a thermostat.

Once the length of the box is set, the system is first run in an *NVT* ensemble where the temperature is controlled by a Nose-Hoover (NH) thermostat. The code used to generate heat flux data is an extension to the *NVT* code used in the course homework. The system is equilibrated at a constant temperature for 300,000 time-steps. Throughout the *NVT* simulation, the heat flux data is not calculated.

Figure 2: Process flow of how heat flux data is computed and collected.

After the allotted 300,000 steps, the system shifts to an *NVE* ensemble. This is done by, setting the value of η (from the NH algorithm) to zero. The system is then equilibrated to a constant energy after running it for 200,00 time-steps. The total energy is conserved within 0.005 % which is acceptable for the system to consider to be at an energy equilibrium.

After both temperature and energy equilibrium is maintained, the production simulation is run. The system is still at *NVE* and heat flux data is collected for 1,000,000 time-steps. It is not computed for every time-step, but rather once every 5 steps. The calculation of heat flux (in all three directions) requires some major modifications to the structure of the code. The forces are first calculated as usual, using these current forces, the velocity is updated. However, there is another loop which is added to calculate the second component of heat flux, $\frac{1}{2}\sum_{i,j}\left(F_{ij}v_i\right)r_{ij}$ in equation mentioned above. The first component is calculated in the outermost loop (main time loop) using the individual kinetic and potential energy to give the site energy, E_i.

This heat flux calculated by implementing the process mentioned above was then later sent to another code that implements the Green-Kubo algorithm to calculate the HCACF and thermal conductivity. The equation mentioned above used to compute these quantities can be discretized into a nested loops. The discretized Green Kubo equation is given by,

$$\mathrm{k} = \frac{\Delta t}{3Vk_BT^2}\sum_{m=1}^{M}\frac{1}{N-m}\sum_{n=1}^{N-m}q(m+n)q(n)$$

Where N is the time origins, which is the ratio of the total timesteps of heat flux data to the sample intervals, which is 5. Thus, for all our simulations, N is 200,000. M is the correlation length which is set to 2,000. The nested loop calculates the time dependent HCACF and multiplying these constants gives a time dependent thermal conductivity, k.

The aim of this project is to reproduce the results generated by McGaughey, A. J. H., & Kaviany, M. (2004), at least for higher temperatures. We will be comparing the plots produced in that paper to what we get via our simulations. Heat flux data is collected for simulations that are run for 70, 80 and 90 K. There were a few concerns about the system at 70 K being either a liquid or a solid. We managed to visualize and see that Argon at 70 K still had liquid behavior. Figure 3 shows a snapshot of one of the frames from the simulation at 70 K using VMD.

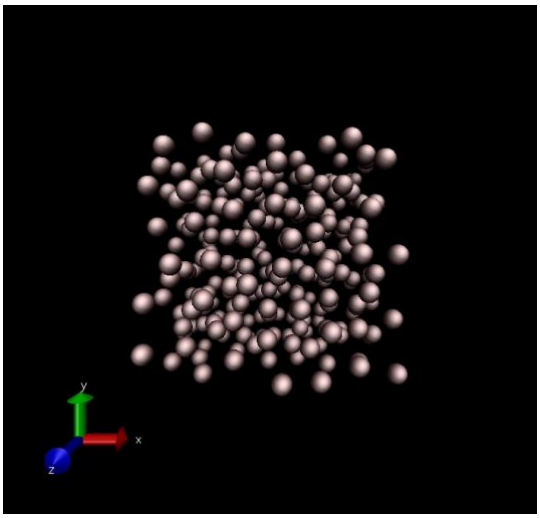

Figure 3: Visualization of Argon at 70 K to demonstrate that it is still in the liquid phase.

Results and Discussions

1. Heat current autocorrelation function (HCACF)

The HCACF is calculated from the procedure mentioned above where its integral is a part of calculating the thermal conductivity of the system. The quantity that is measured is time dependent and is expected to decorrelate as time tends to infinity. As per McGaughey, A. J. H., & Kaviany, M. (2004), the HCACF is supposed to have a slight sensitivity to temperature (for liquids). Figure 4 shows the plot that is made in their paper. The y axis is the HCACF normalized by the autocorrelation of the first timestep and the x-axis is the correlation length (M). According to Figure 4, normalized HCACF for liquids is supposed to start from 1.0 and then gradually decorrelate with after 1.0 ps of correlation time.

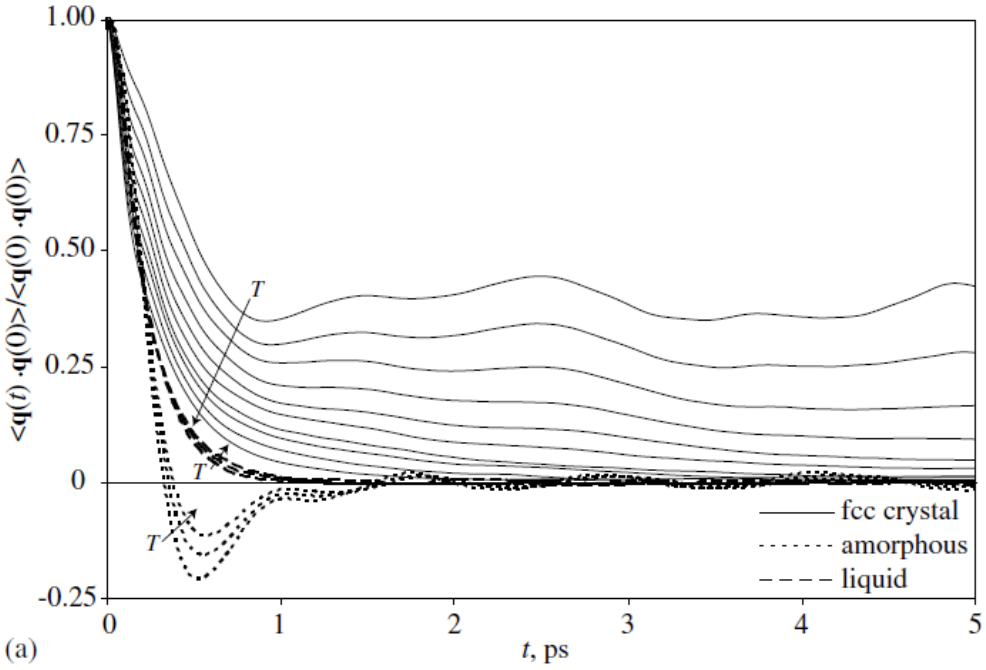

Figure 4: Time dependence of the raw HCACF for all cases considered, i.e., solid, amorphous, and liquid from McGaughey, A. J. H., & Kaviany, M. (2004) . Our results are being compared with the liquid curves.

These plots show that as the temperature of liquid argon increases the unsteady HCACF also increases. To make sure that the simulations that we ran are reasonably good, our plots of HCACF must also produce very similar profiles. Figure 5 shows these profiles for the three temperatures 70, 80 and 90 K. They appear consistent to the liquid phase plots in Figure 4. The HCACF decorrelates after 1 ps of correlation time. A zoomed in plot is shown in Figure 5 which shows that the magnitude of HCACF slightly increases with temperature. This increase might not seem significant, but it is consistent with Figure 4.

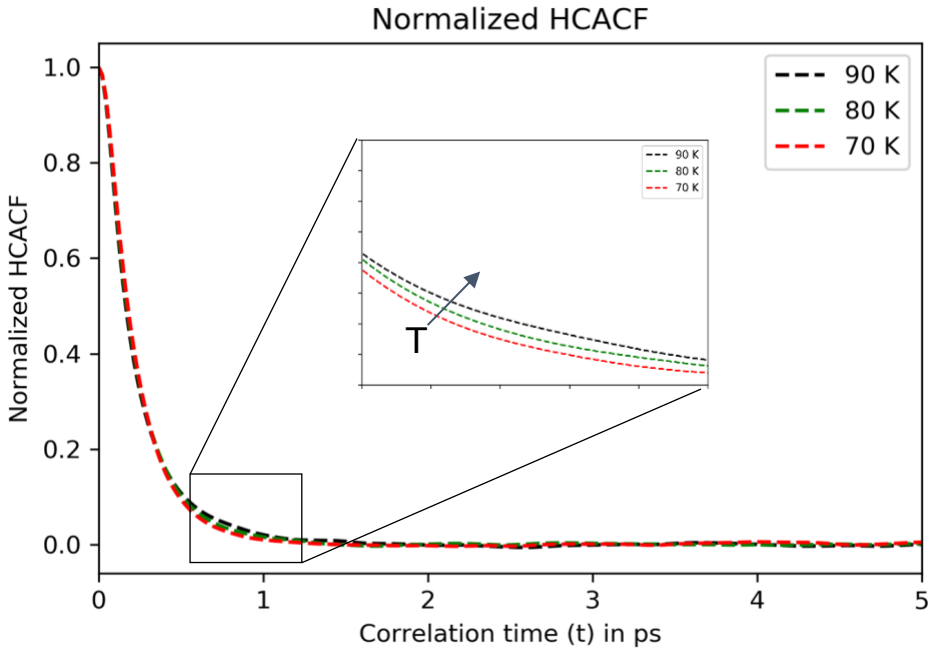

Figure 5: Plot of normalized HCACF vs correlation time for different liquid temperatures. A tiny portion of the curve is zoomed in to observe temperature dependence.

2. Thermal conductivity

The thermal conductivity is calculated by using the HCACF results. The plots from the paper are shown in Figure 6, where the curves of concern are only the liquid ones. They are seen to increase from zero and then stabilize after about 1.0 ps of correlation time. There even seems to be an observable decrease in the value of thermal conductivity with temperature. Our results are plotted in Figure 7 for 70, 80 and 90 K. The curves stabilize to an equilibrium thermal conductivity at around 1 ps, like the plot from the paper. The temperature dependence on thermal conductivity is also consistent to that produced in Figure 6.

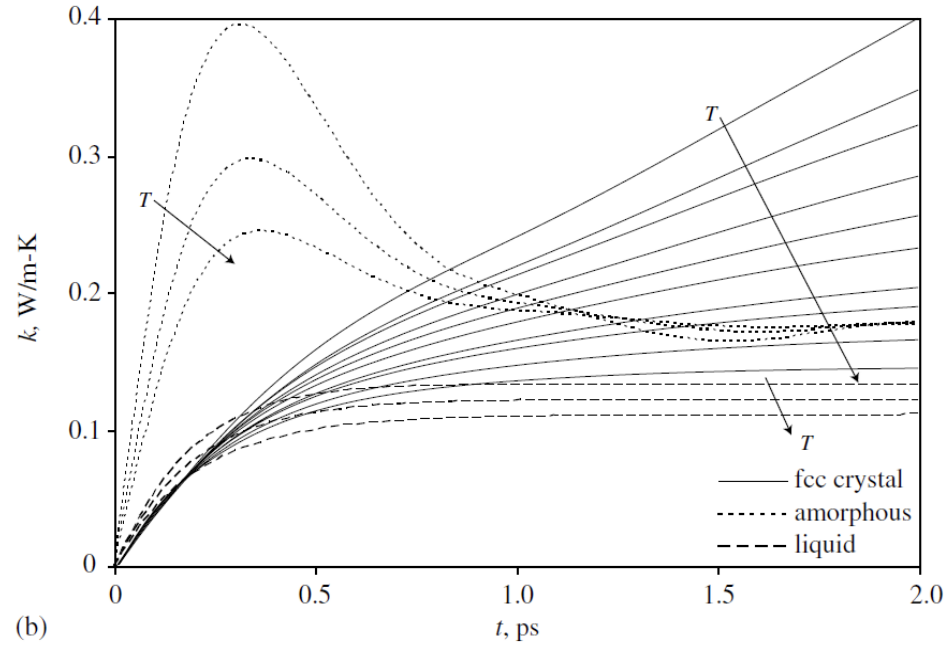

Figure 6: Plot of thermal conductivity, k vs correlation time in ps for all cases considered, i.e., solid, amorphous, and liquid from McGaughey, A. J. H., & Kaviany, M. (2004) . Our results are being compared with the liquid curves.

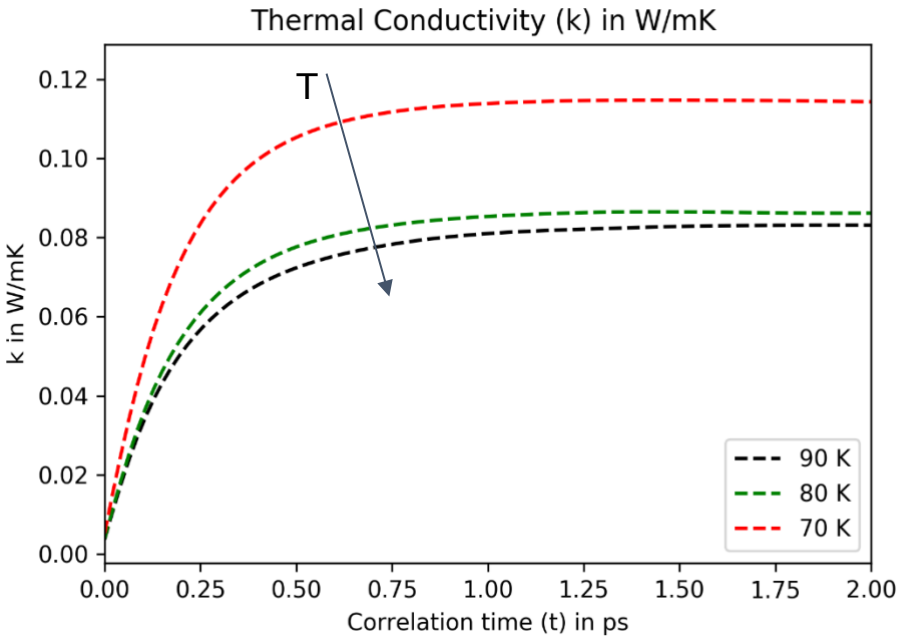

Figure 7: Plot of thermal conductivity vs correlation time in ps for different liquid temperatures.

Table 1 shows the equilibrium thermal conductivity for each temperature and also the density of the system that corresponds to an almost-zero pressure.

Table 1: Equilibrium thermal conductivity for liquid argon at different temperatures and densities that correspond to near-zero pressures.

Temperature (K)	Density (kg/m^3)	k (W/mK)
70	1356	0.115
80	1233	0.086
90	1187	0.082

These values are not the same as what is found in the paper. There are two reasons for why such a change is observed, (1) use of a different cutoff scheme as compared to the one that was implemented in the homework as well as this code and (2) is running the system in an *NpT* before data collection to make sure the pressure is exactly set is 0 Pa.

Conclusion

The use of Green Kubo method has proven to be useful in computing thermal properties at an atomistic level. Quantities like thermal conductivity play a major role to give insights into a material that cannot be obtained through experiments. The simplicity of the Green-Kubo algorithm and the Lennard-Jones potential makes writing code to calculate the thermal conductivity of argon less hard of a task. We were successful in reproducing the trends of heat current autocorrelation function (HCACF) and thermal conductivity of liquid argon in comparison to previously published results.

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