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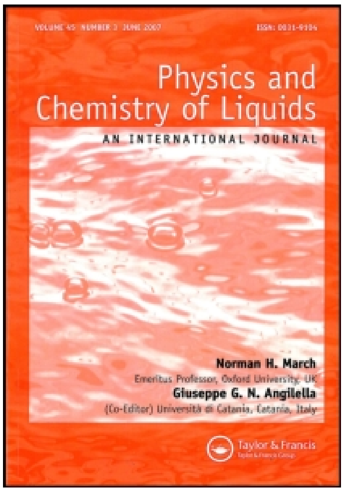

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Self Diffusion Coefficient and Force Auto-Correlation Function

Rajneesh K. Sharma[a]; K. N. Pathak[a]; K. Tankeshwar[b]; S. Ranganathan[c]
[a] Centre of Advanced Study in Physics, Punjab University, Chandigarh, India [b] Department of Physics, H.P. University, Shimla, India [c] Department of Mathematics and Computer Science, Royal Military College, Kingston, Ontario, Canada

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SELF DIFFUSION COEFFICIENT AND FORCE AUTO-CORRELATION FUNCTION

RAJNEESH K. SHARMA and K. N. PATHAK

*Centre of Advanced Study in Physics, Punjab University,
Chandigarh-160 014, India*

K. TANKESHWAR

Department of Physics, H.P. University, Shimla-171 005, India

S. RANGANATHAN

*Department of Mathematics and Computer Science,
Royal Military College, Kingston, Ontario, Canada K7K 5LO*

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Self diffusion coefficients of the Lennard-Jones fluid have been calculated using a model for the force auto-correlation function. Parameters of the proposed model are determined using frequency sum rules of the velocity auto-correlation function. Predicted results for the self diffusion coefficient are found to be in a reasonable agreement with computer simulation data.

KEY WORDS: Velocity auto-correlation function, self diffusion coefficient, memory function.

1 INTRODUCTION

The velocity auto-correlation function (VACF) which is a microscopic manifestation of the self diffusion coefficient is a fundamental quantity in the study of dynamics of a single particle in a condensed many body system. It contains information about the motion of a tagged particle under the influence of all other particles in the system. The exact evaluation of the time evolution of the VACF is a complicated many body problem except for very simple cases of atomic motions. However, one can obtain useful information about its time evolution from the Mori's memory function formalism[1,2]. In fact, the memory function has played a key role in theoretical calculations of time correlation functions and transport coefficients[1]. The microscopic expression of the memory function involves the dynamics of projected Liouville operator which is difficult to calculate exactly for a many body system. However, on dropping the projection operator in the expression of memory function of the VACF one obtains a function called force auto-correlation (FACF). Within the projection operator technique used in deriving the Mori equation, there exists an exact relation between the FACF and the memory function. Therefore, one expects that FACF plays the somewhat similar role as that of a memory function in studying the dynamics of fluids. Thus, our problem of calculating VACF or self diffusion coefficient reduces to the problem of calculating FACF. The FACF is a time correlation function, microscopic force and hence it can be exactly evaluated[3,4] using computer simulation technique unlike the memory function. The FACF can also be approximately calculated by performing the microscopic calculations. Recently, the FACF has been calculated by Pathak *et al.*,[5] in the low density limit by taking into account only the binary collision. But it is not yet possible to calculate it for dense fluids. On the other hand, one can model the FACF in a similar way as one models the memory function. Therefore, in this paper we propose a model for the FACF to examine the utility of this approach by comparing results thus obtained for the self diffusion coefficient with computer simulation results[3,6] over the entire fluid range.

The layout of the paper is as follows. In section 2 we have presented theory and model. Results and discussion are given in section 3. Conclusion is given in section 4.

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2 THEORY

2.1 *Generalities*

The velocity auto-correlation function (VACF) $\psi(t)$, which is defined as

$$\psi(t) = \langle v_{1x}(0)\, v_{1x}(t) \rangle / \langle v_{1x}^2(0) \rangle \tag{1}$$

and is related to the self diffusion coefficient through the Green Kubo expression given as

$$D = \frac{k_B T}{m} \int_0^\infty \psi(t)\, dt. \tag{2}$$

In the above equation, $v_{1x}(t)$ is the x-component of the velocity of particle 1 at time t. And k_B, T and m are the Boltzmann constant, temperature and atomic mass of the particle. The exact evaluation of VACF and hence of self diffusion coefficient is not yet feasible except for very simple cases of models of fluid. However, at the molecular level the time evolution of the VACF can be obtained by using the generalised Langevin equation:

$$\frac{\partial \psi(t)}{\partial t} = -\int_0^t K(t-t')\, \psi(t')\, dt', \tag{3}$$

where $K(t)$ is a memory function defined as

$$K(t) = \langle \dot{v}_{1x}(0) \exp[i(1-P)Lt]\, \dot{v}_{1x}(0) \rangle / \langle v_{1x}^2(0) \rangle, \tag{4}$$

with P and L as the projection and Liouville operators, respectively. Differentiating Eq. (3) we get

$$\ddot{\psi}(t) = -K(t) - \int_0^t dt'\, K(t-t')\, \dot{\psi}(t'), \tag{5}$$

where $\ddot{\psi}(t)$ is the second derivative of $\psi(t)$ w.r.t. time t.

Dropping projection operator in Eq. (4) we obtain expression for the force auto-correlation function (FACF) given as

$$\phi(t) = \langle \dot{v}_{1x}(0) \exp(iLt)\, \dot{v}_{1x}(0) \rangle / \langle [v_{1x}(0)]^2 \rangle = -\ddot{\psi}(t) \tag{6}$$

Using Eq. (6) in Eq. (5), we obtain a relation among VACF, FACF and the memory function given as

$$k(t) = \phi(t) - \int_0^t dt'\, K(t-t')\, \dot{\psi}(t'). \tag{7}$$

From the above equation it is clear that for $t = 0$, $K(t)$ and $\phi(t)$ are identical. It is also seen that for short times the behaviour of $K(t)$ and $\phi(t)$ cannot differ greatly as the contribution from the integral remains small. Therefore, the approximation $K(t) \simeq \phi(t)$ could be very effective in representing the essential short time features of $K(t)$.

Defining Fourier-Laplace transform as

$$\tilde{\psi}(\omega) = i \int_0^\infty \exp(i\omega t)\, \psi(t)\, dt, \tag{8}$$

we obtain from Eq. (3)

$$\tilde{\psi}(\omega) = \frac{-\psi(0)}{\omega + \tilde{K}(\omega)}, \tag{9}$$

where $\tilde{K}(\omega)$ is the Fourier-Laplace transform of the memory function $K(t)$. Similarly, taking the Fourier-Laplace transform of Eq. (5) we obtain

$$\tilde{\phi}(\omega) = -\omega\, \tilde{\psi}(\omega)\, \tilde{K}(\omega). \tag{10}$$

Eliminating $\tilde{\psi}(\omega)$ from Eqs. (9) and (10) we obtain a relation between memory function and FACF in ω-space given as

$$\tilde{K}(\omega) = \frac{\omega\, \tilde{\phi}(\omega)}{\omega - \tilde{\phi}(\omega)}. \tag{11}$$

Writing

$$\tilde{\phi}(\omega) = \phi'(\omega) + i\phi''(\omega) \tag{12}$$

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where $\phi'(\omega)$ and $\phi''(\omega)$ represent real and imaginary parts of $\tilde{\phi}(\omega)$, we obtain expressions for the real and imaginary parts of $\tilde{K}(\omega)$, given as

$$K'(\omega) = \frac{\omega^2\phi'(\omega) - \omega(\phi'^2(\omega) + \phi''^2(\omega))}{(\omega - \phi'(\omega))^2 + \phi''^2(\omega)} \tag{13a}$$

and

$$K''(\omega) = \frac{\omega^2(\phi''(\omega))}{(\omega - \phi'(\omega))^2 + \phi''(\omega)^2}. \tag{13b}$$

The memory function in time domain is readily obtained from the following expression:

$$K(t) = \frac{2}{\pi}\int_0^\infty \cos(\omega t)\, K''(\omega)\, d\omega. \tag{14}$$

Defining the frequency spectrum of $f(\omega)$ of the VACF as

$$f(\omega) = 2\,\psi''(\omega) = 2\int_0^\infty \cos(\omega t)\,\psi(t)\, dt, \tag{15}$$

where $\psi''(\omega)$ is the imaginary part of $\tilde{\psi}(\omega)$. The expression for the $\psi''(\omega)$ is obtained from Eq. (9) by writing $\tilde{K}(\omega) = K'(\omega) + iK''(\omega)$ and is given by

$$\psi''(\omega) = \frac{K''(\omega)}{(\omega + K'(\omega))^2 + (K''(\omega))^2}. \tag{16}$$

The time evoluation of $\psi(t)$ can be obtained from

$$\psi(t) = \frac{1}{\pi}\int_0^\infty \cos(\omega t)\, f(\omega)\, d\omega. \tag{17}$$

The expression for the self diffusion coefficient obtained from Eqs. (2) and (15) is given as

$$D = \frac{k_B T}{m} f(0)/2 = \frac{k_B T}{m}\,[K''(0)]^{-1}. \tag{18}$$

In the next subsection we propose a model for the FACF.

2.2 *Model for the Force Auto-Correlation Function*

It is seen from the preceding sub-section that $K(t)$ or $\phi(t)$ are basic quantities in the evaluation of the VACF or the self diffusion coefficient. It is due to the fact that one

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can introduce model calculations or phenomenological forms for $K(t)$ or $\phi(t)$ and can still preserve number of properties of the velocity auto-correlation functions. This has already been well understood[1,7] for the calculation of time correlation function by modeling the memory function. But till now there exist only few studies in which one approximate the FACF to calculate the VACF. In the past the FACF has been studied using the computer simulation technique[3,4] as well as by performing microscopic calculations[5]. It has been demonstrated by recent microscopic calculations[5], which are based on determining the binary collision contribution to it, that theoretical FACF does not satisfy its exact properties which are given as

$$\int_0^\infty dt\,\phi(t)=0 \quad \text{and} \quad \int_0^\infty dt\,t\phi(t)=-1, \tag{19}$$

but still provides a reasonable estimate of the self diffusion coefficient. Therefore, it is expected that a simple phenomenological model for $\phi(t)$ will provide a useful estimate of the self diffusion coefficient. We propose a phenomenological form for $\phi(t)$ given as

$$\phi(t)=\phi(0)\exp(-\beta t^2)\cos(bt), \tag{20}$$

with its short time expansion:

$$\phi(t)=\phi(0)\left[1-\frac{t^2}{2}(b^2+2\beta)+\cdots\cdots\right]. \tag{21}$$

Taking the Fourier-Laplace transform of Eq. (20) and separating real and imaginary parts, we have[8]

$$\begin{aligned}\phi'(\omega)=-\frac{1}{2}\Bigg[&\frac{(\omega+b)}{2\beta}\sum_{K=1}^{\infty}\frac{1}{(2K-1)!!}\left\{\frac{-(\omega+b)^2}{2\beta}\right\}^{K-1}\\&+\frac{(\omega-b)}{2\beta}\sum_{K=1}^{\infty}\frac{1}{(2K-1)!!}\left\{\frac{-(\omega-b)^2}{2\beta}\right\}^{K-1}\Bigg]\end{aligned} \tag{22}$$

$$\phi''(\omega)=\frac{1}{4}\sqrt{\frac{\pi}{\beta}}\left[\exp\frac{-(\omega-b)^2}{4\beta}+\exp\frac{-(\omega+b)^2}{4\beta}\right]. \tag{23}$$

Two parameters of Eq. (20) are obtained by comparing Eq. (21) with the short time expansion of $\phi(t)$ given as

$$\phi(t)=V_2\left[1-\frac{t^2}{2!}\frac{V_4}{V_2}+\cdots\right], \tag{24}$$

we obtain

$$\phi(0) = V_2 \quad \text{and} \quad b^2 + 2\beta = V_4/V_2. \tag{25}$$

Further, we assume that the FACF oscillates with Einstein frequency equal to $\sqrt{V_2}$. This sets one of the parameters of $\phi(t)$ i.e., $b^2 = V_2$ and hence $\beta = \frac{1}{2}((V_4/V_2) - V_2)$.

Since the model FACF does not satisfy its exact properties (Eq. (19)), it yields unphysical results for the self diffusion coefficient obtained by using Eq. (13) and (18). Therefore, we assume[5] that $K(t) = \phi(t)$ for all times and hence obtain an expression for self diffusion coefficient given by

$$D = \frac{k_B T}{m} [\phi''(0)]^{-1}$$

$$= \sqrt{\frac{2}{\pi}} \frac{k_B T}{m} \frac{((V_4/V_2) - V_2)^{1/2}}{V_2} \exp\left(\frac{V_2^2}{2(V_4 - V_2^2)}\right). \tag{26}$$

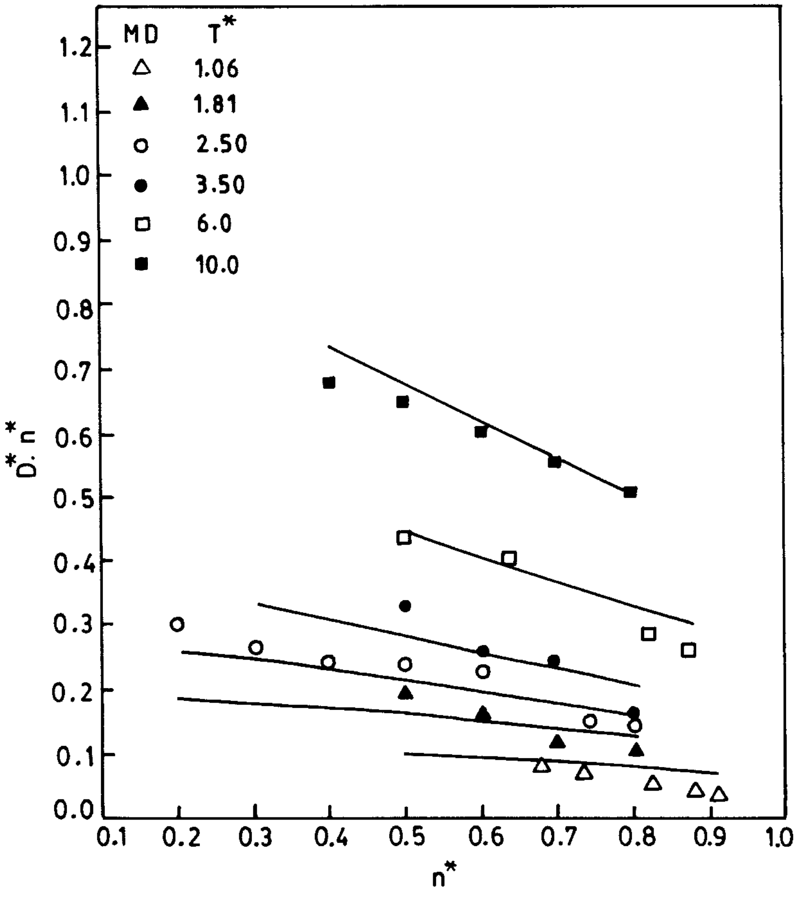

Figure 1 Variation in the self diffusion coefficients with density at various temperatures. Solid lines represent our results.

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3 RESULTS AND DISCUSSION

In order to calculate the self diffusion coefficient from Eq. (26) we require V_2 and V_4 as input. General expressions for these are given by Tankeshwar *et al.*,[9] (1987). The calculation of V_2 involves only the static pair correlation function whereas V_4 involves both static pair and triplet correlation functions along with the interatomic potential. Due to limited information about static triplet correlation function the superposition approximation has been used. The validity of the superposition approximation has been checked in work of Tankeshwar, Pathak and Ranganathan[7]. It was noted that the use of superposition approximation does not introduce significance error in the calculation of the sum rules. In the present work, we use our earlier results[9] of sum rules to calculate the self diffusion coefficient of LJ fluids using Eq. (26). Results obtained for the self diffusion coefficient $D^* = D(m/\varepsilon\sigma)^{1/2}$; where σ and ε are two parameters of LJ fluids, are plotted in Figure 1 as a function of density, $n^*(=n\sigma^3)$ for six isotherms. The MD results of Heyes[3,6] are also shown there. The temperature dependence of the self diffusion coefficient is presented in Figure 2 for six densities along with the computer simulation data[3,6]. It can be seen from Figures 1 and 2 that a good agreement is obtained at temperature above the critical temperature and densities below the triple point density. Results of the self diffusion coefficient at the triple point is almost twice as that of the computer

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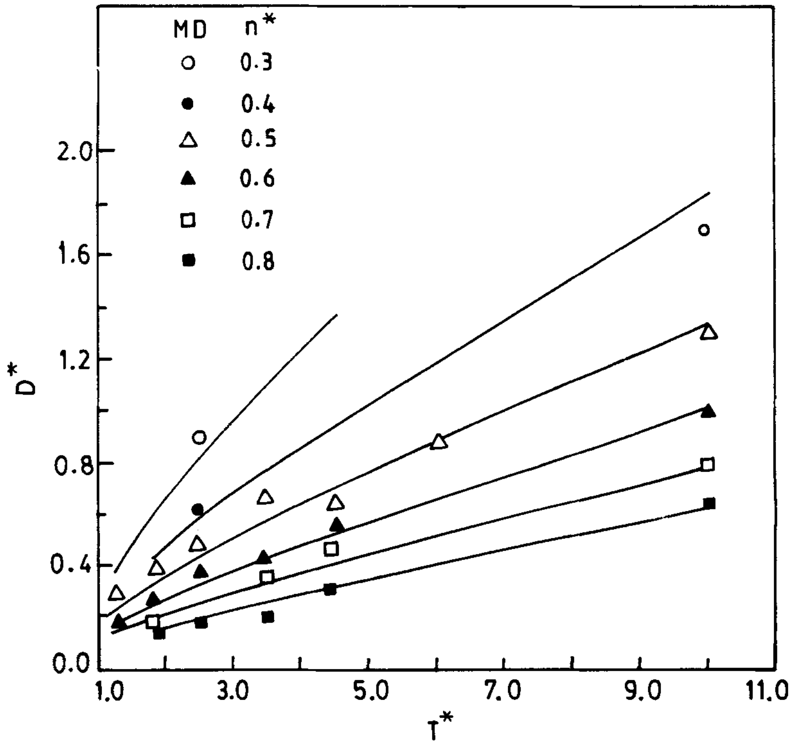

Figure 2 Variation in the self diffusion coefficients with temperature. Solid lines are our results.

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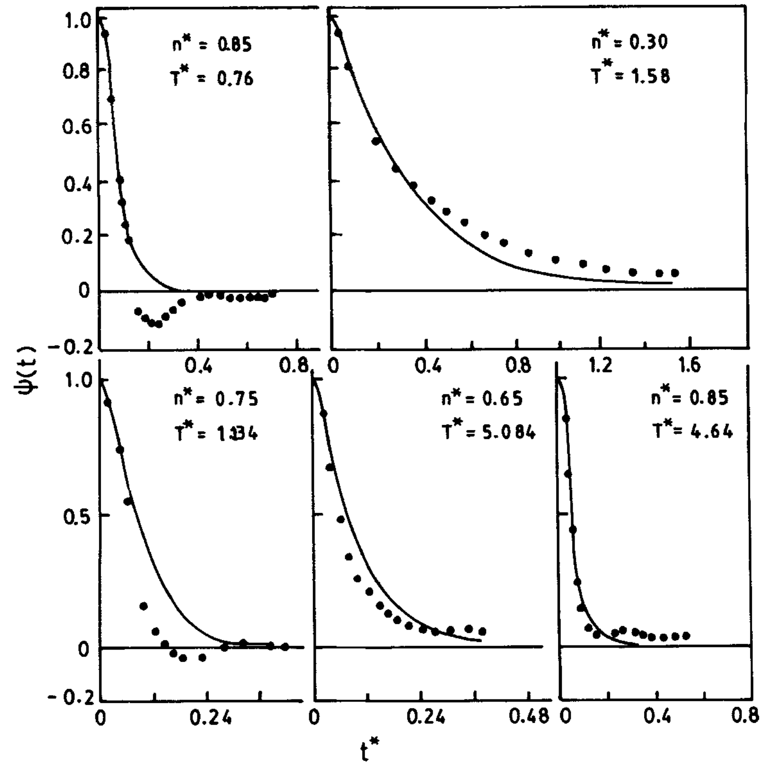

Figure 3 Variation in the normalized VACF $\psi(t)$ with time $t^* = t(\varepsilon/m\sigma^2)^{1/2}$ obtained for five thermodynamic states of LJ fluids. Solid lines are our results whereas full circles represent MD data.

simulation data. This is an expected result as our model does not satisfy the properties of the FACF given by Eq. (19) and further the approximation $K(t) = \phi(t)$ is valid only at short times. Thus, our model does not include the correct intermediate and long time behaviour of $\psi(t)$ which play an important role in determining the self diffusion coefficient of dense fluids. This can be examined by studying the time evolution of $\psi(t)$.

We calculate the time evolution of $\psi(t)$ from Eq. (17) using $K(t) = \phi(t)$ in Eq. (16). Results obtained are shown as continuous curves in Figure 3 for five thermodynamic states. Simulation results of Kushick and Berne[10] and of Lee and Chung[11] are also shown there as solid circles. From Figure 3 it is seen that our model reproduces the short time behaviour of the VACF. At intermediate and long times the best agreement is obtained only at the lowest density investigated here. This is consistent with our finding of self diffusion coefficient.

It is also of interest to see the behaviour of $K(t)$ obtained from Eqs. (13) and (14). Since we expect good results only for the low density fluid, results obtained for $K(t)$ at the lowest density investigated here are shown as solid circles in Figure 4. Corresponding simulation results[10] of $K(t)$ are also shown there as a continuous line. It

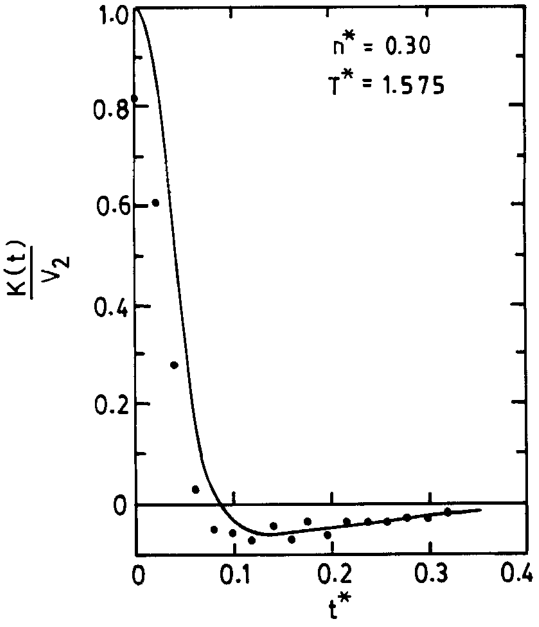

Figure 4 Variation of memory function $K(t)/V_2$ with time $t^* = t(\varepsilon/m\sigma)^{1/2}$. Full circles are our results whereas solid line represent molecular dynamics results.

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can be seen from Figure 4 that the model calculation provides $K(0) \neq \phi(0)$ which has also been noted by Pathak *et al.*[5] However, our model predicts a reasonable agreement with simulation results at large times.

4 SUMMARY AND CONCLUSION

In this paper we have studied the dynamics of a tagged particle and calculated the self diffusion coefficient using a simple model for the FACF. It is found that results obtained for the self diffusion coefficients are in agreement with computer simulation data for a wide fluid range except for the densities and temperatures which are close to the triple point. The disagreement near the triple point may be due to the fact that our proposed model for the FACF does not satisfy its exact properties and therefore can be valid only in the low density limit. The study presented here is expected to be useful in further modeling the FACF and in studying the friction coefficient of Brownian type particles.

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