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# Anisotropic spatially heterogeneous dynamics in a model glass-forming binary mixture

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## Abstract

We calculated a four-point correlation function $G_4(\vec{k}, \vec{r}; t)$ and the corresponding structure factor $S_4(\vec{k}, \vec{q}; t)$ for a model glass-forming binary mixture. These functions measure the spatial correlations of the relaxation of different particles. We found that these four-point functions are anisotropic and depend on the angle between vectors $\vec{k}$ and $\vec{r}$ (or $\vec{q}$). The anisotropy is the strongest for times somewhat longer than the $\beta$ relaxation time, but it is quite pronounced even for times comparable to the $\alpha$ relaxation time, $\tau_\alpha$. At the lowest temperatures $S_4(\vec{k}, \vec{q}; \tau_\alpha)$ is strongly anisotropic even for the smallest wavevector $q$ accessible in our simulation.

## 1. Introduction

The hypothesis that there is a growing dynamical correlation length which accompanies the glass transition, and that this correlation length is associated with the dramatic slowing down of the dynamics of a supercooled liquid, has recently prompted many computational and theoretical investigations [1–9] and some experimental studies [10, 11]. Several studies have been motivated by the observation that the relaxation of the supercooled liquid involves the correlated motion of clusters of particles, and the size of the clusters increases with decreasing temperature [12]. Since two-point correlation functions, for example the van Hove correlation function, do not provide any information about the spatial correlations of particle relaxation, four-point correlation functions were introduced. The dynamic correlation length was determined by studying the spatial decay of these four-point correlation functions (or the small wavevector dependence of their Fourier transforms), and several studies have found that this dynamic correlation length increases with decreasing temperature [1, 3, 6, 13].

The four-point correlation functions are usually assumed to be isotropic (in some cases they are isotropic by construction [3]). However, several researchers have noted that on the $\beta$ relaxation timescale the correlated motion of particles is not isotropic. Doliwa and Heuer [14]

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observed pronounced anisotropy in the $\beta$ relaxation regime for a hard sphere system. Glotzer *et al* reported that the motion of 'mobile' particles for a model binary Lennard-Jones liquid is not isotropic but the particles move in patterns which they referred to as 'string-like' [15, 16]. In other words, the motion of particles in the liquid would be strongly coupled along quasi-one-dimensional 'strings'. These observations suggest that the correlated motion of the molecules of the liquid is anisotropic during $\beta$ relaxation. Therefore, an appropriately defined four-point correlation function used to measure this motion should also be anisotropic, at least in the $\beta$ relaxation regime. In this paper we discuss a four-point correlation function and the corresponding structure factor which are anisotropic on the timescale of *both* $\beta$ and $\alpha$ relaxation.

## 2. Simulation

To calculate the four-point correlation function and the corresponding structure factor we use the trajectories generated in an earlier [17, 18] extensive Brownian dynamics simulation study of a 80:20 Lennard-Jones binary mixture introduced by Kob and Andersen [19]. Briefly, $N = 1000$ particles were simulated in a cubic box of length 9.4 $\sigma_{AA}$, using the interaction potential $V_{\alpha\beta} = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$, where $\alpha, \beta \in \{A, B\}$, and $\epsilon_{AA} = 1.0, \epsilon_{AB} = 1.5$, $\epsilon_{BB} = 0.5$, $\sigma_{AA} = 1.0$, $\sigma_{AB} = 0.8$ and $\sigma_{BB} = 0.88$. The details of the simulations are described in [17, 18]. We only present results for the larger and more abundant A particles. Thus, all sums over particles in the formulae below run over the A particles only. In the figures we present the distance as $r/\sigma_{AA}$, the wavevector dependence as $q\sigma_{AA}$ and the time as $tD_0/\sigma_{AA}^2$; $D_0$ is the short time diffusion coefficient, which is temperature dependent in our simulations. The temperature is expressed in units of $\epsilon_{AA}/k_{\rm B}$.

## 3. Four-point correlation function

A four-point correlation function that we study characterizes correlations between the relaxation of different particles. Consider the function

$$\hat{F}_n(\vec{k}; t) = {\rm e}^{-{\rm i}\vec{k}\cdot[\vec{r}_n(t)-\vec{r}_n(0)]}, \tag{1}$$

where $\vec{r}_n(t)$ is the position of particle $n$ at a time $t$. The ensemble average of $\hat{F}_n(\vec{k}; t)$ is equal to the self-intermediate scattering function $F_s(k; t)$,

$$\langle \hat{F}_n(\vec{k}; t)\rangle = F_s(k; t). \tag{2}$$

The four-point function $G_4$ measures correlations between the microscopic self-intermediate functions pertaining to different particles separated at $t = 0$ by vector $\vec{r}$ (see figure 1),

$$G_4(\vec{k}, \vec{r}; t) = \frac{V}{N^2} \sum_{n\neq m} \langle \hat{F}_n(\vec{k}; t)\hat{F}_m(-\vec{k}; t)\delta[\vec{r} - \vec{r}_{nm}(0)]\rangle, \tag{3}$$

where $\vec{r}_{nm} = \vec{r}_n - \vec{r}_m$, $V$ is the volume and $N$ is the number of particles. In this work we fixed $|\vec{k}| = 7.25$, which is around the value of the first peak in the static structure factor [18][2]. Note that $G_4(\vec{k}, \vec{r}; 0) = g(r)$ where $g(r)$ is the pair correlation function.

The microscopic self-intermediate functions $\hat{F}_n(\vec{k}; t)$ are sensitive to the motion of particles along the wavevector $\vec{k}$. Thus, the four-point function $G_4(\vec{k}, \vec{r}; t)$ measures correlations between the motion of particles along $\vec{k}$. We expect that for small values of $|\vec{r}|$ the anisotropy of these correlations is most pronounced for $\vec{r}$ parallel to $\vec{k}$.

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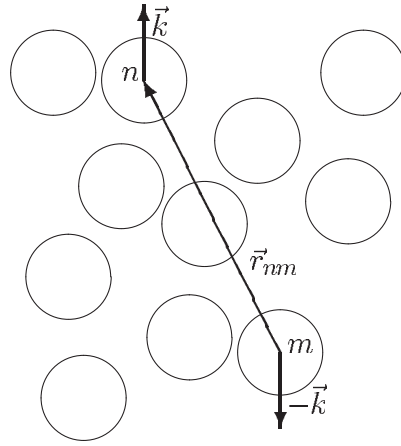[2] The susceptibility $\chi_4(k; t)$ depends non-trivially on $k$, see [20].

**Figure 1.** $G_4(\vec{k}, \vec{r}; t)$ is a pair correlation function in which contributions of the individual particles are weighted by their microscopic self-intermediate functions $\hat{F}_n(\vec{k}; t)$.

To investigate local correlations on the $\alpha$ relaxation timescale[3] we expanded $G_4(\vec{k}, \vec{r}; t)$ into the Legendre polynomials,

$$G_4(\vec{k}, \vec{r}, t) = \sum_n L_n(k, r; t) P_n(\hat{\vec{k}} \cdot \hat{\vec{r}}) \tag{4}$$

where $P_n$ is the $n$th Legendre polynomial, $\hat{\vec{k}} = \vec{k}/k$, $\hat{\vec{r}} = \vec{r}/r$, and

$$L_n(k, r; t) = \frac{2n+1}{4\pi} \int G_4(\vec{k}, \vec{r}, t) P_n(\hat{\vec{k}} \cdot \hat{\vec{r}}) \, d\hat{\vec{r}}. \tag{5}$$

In equation (5) $d\hat{\vec{r}}$ denotes integration over a unit sphere. If $G_4(\vec{k}, \vec{r}; t)$ does not depend on the angle between $\vec{k}$ and $\vec{r}$, then $L_n(k, r; t)$ will be zero for $n > 0$. Note that the imaginary part of $G_4(\vec{k}, \vec{r}; t)$ is not zero, thus there are non-zero real and imaginary parts to $L_n(k, r; t)$; by symmetry, the imaginary part of $L_n(k, r; t)$ is identically zero for even $n$, and the real part is zero for odd $n$.

In figure 2 we present results for $L_0(k, r; \tau_\alpha)$, Im $L_1(k, r; \tau_\alpha)$ and $L_2(k, r; \tau_\alpha)$ where $\tau_\alpha$ is the $\alpha$ relaxation time (see footnote 3). As expected, even on this long timescale there are strong local correlations between the relaxation of particles. The height of the first peak of the isotropic component of $G_4$, $L_0(k, r; \tau_\alpha)$, increases with decreasing temperature. Furthermore, we find pronounced anisotropy of the local correlations. The correlations revealed by $G_4(\vec{k}, \vec{r}; \tau_\alpha)$ are the strongest when vectors $\vec{k}$ and $\vec{r}$ are parallel. The amplitude of the anisotropic part of $G_4(\vec{k}, \vec{r}; \tau_\alpha)$ is, roughly speaking, temperature independent for $T \leqslant 1.0$.

## 4. Four-point structure factor

To examine correlations between particle relaxation for large distances we turn to the structure factor corresponding to the four-point correlation function, $S_4(\vec{k}, \vec{q}; t)$:

$$S_4(\vec{k}, \vec{q}; t) = 1 + (N/V) H_4(\vec{k}, \vec{q}; t), \tag{6}$$

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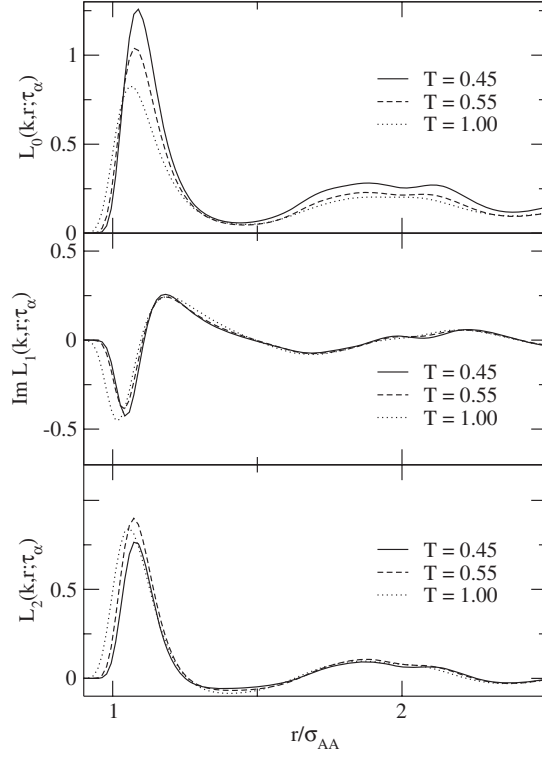[3] The $\alpha$ relaxation time is defined to be when $F_s(\vec{k}; \tau_\alpha) = e^{-1}$, where $|\vec{k}| = 7.25$.

**Figure 2.** The projections $L_0(k, r; \tau_\alpha)$, Im $L_1(k, r; \tau_\alpha)$ and $L_2(k, r; \tau_\alpha)$ for $T = 0.45$, 0.55, and 1.00.

where $H_4(\vec{k}, \vec{q}; t)$ is the Fourier transform of $G_4(\vec{k}, \vec{r}; t) - F_s^2(k; t)$. For $\vec{q} \neq \vec{0}$ we have

$$S_4(\vec{k}, \vec{q}; t) = \frac{1}{N} \sum_{n,m} \langle \hat{F}_n(\vec{k}; t) \hat{F}_m(-\vec{k}; t) e^{-i\vec{q} \cdot \vec{r}_{nm}(0)} \rangle. \tag{7}$$

Four-point wavevector-dependent functions similar to $S_4(\vec{k}, \vec{q}; t)$, usually evaluated at $t = \tau_\alpha$, have been used previously to determine dynamic correlation lengths [1, 7, 9].

First, in figure 3 we examine projections of $S_4(\vec{k}, \vec{q}; t)$ onto the Legendre polynomials,

$$I_n(k, q; t) = \frac{2n + 1}{4\pi} \int S_4(\vec{k}, \vec{q}, t) P_n(\hat{\vec{k}} \cdot \hat{\vec{q}}) \, d\hat{\vec{q}}, \tag{8}$$

at the $\alpha$ relaxation time. We do not show $I_1(k, q; \tau_\alpha)$ since it is small for $q\sigma_{AA} < 5$. Next, in figure 4 we examine $S_4(\vec{k}, \vec{q}; \tau_\alpha)$ for different angles $\theta$ between $\vec{k}$ and $\vec{q}$. In accordance with numerous earlier investigations [1, 2, 5, 6], we find that the large long-range correlations between the relaxation of particles increase with decreasing temperature. Surprisingly, we find that even the long-range correlations on the $\alpha$ relaxation timescale are strongly anisotropic. At low $q$ the correlations are strongest for $\vec{q} \perp \vec{k}$. In direct space this corresponds to strong correlations for particles separated by a vector $\vec{r}$ which is parallel to $\vec{k}$.

The anisotropy of $S_4(\vec{k}, \vec{q}; t)$ makes the determination of a single dynamic correlation length difficult. We tried to fit the low $\vec{q}$ values of $S_4(\vec{k}, \vec{q}; t)$ for a fixed angle $\theta$ between $\vec{k}$ and $\vec{q}$ to several different functional forms, but could not find a form where the results were reasonable for $T < 0.50$. Specifically, fits to an Ornstein–Zernicke formula were very poor. The correlation length determined from the fits was either larger than half the simulation cell,
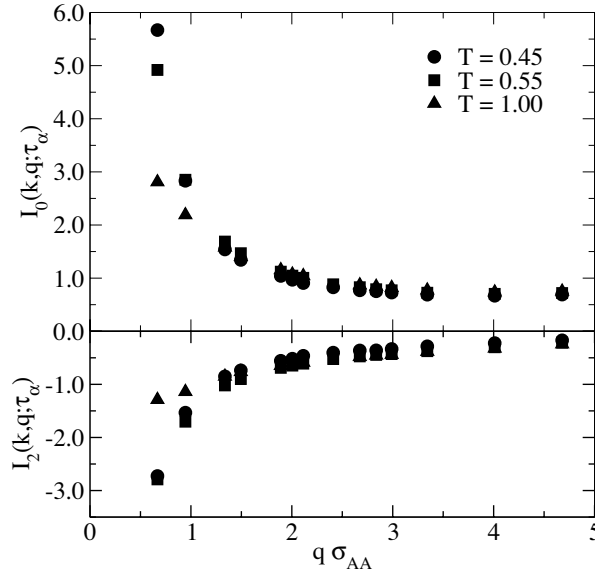
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**Figure 3.** The projections $I_0(k, q; \tau_\alpha)$ and $I_2(k, q; \tau_\alpha)$ for $T = 0.45$, $0.55$ and $1.00$.

or we had to fix the unknown $\vec{q} = \vec{0}$ value of $S_4(\vec{k}, \vec{q}; t)$. Larger systems need to be simulated in order to better understand the low $q$ behaviour of $S_4(\vec{k}, \vec{q}; t)$.

While it has been previously shown that heterogeneous dynamics on the $\beta$ relaxation timescale is anisotropic [14], the strong anisotropy of $S_4(\vec{k}, \vec{q}; \tau_\alpha)$ was a surprise. To investigate the time dependence of the anisotropy we examined the ratio $S_4(\vec{k}, \vec{q}_\perp; t)/S_4(\vec{k}, \vec{q}_\parallel; t)$, where $S_4(\vec{k}, \vec{q}_\perp; t)$ is calculated for the smallest wavevector allowed due to the periodic boundary conditions ($|\vec{q}_\perp| = 2\pi/L$) perpendicular to $\vec{k}$ and $S_4(\vec{k}, \vec{q}_\parallel; t)$ is calculated for the smallest wavevector ($|\vec{q}_\parallel| = 2\pi/L$) parallel to $\vec{k}$. This ratio is shown in figure 5 for $T = 1.0$, $0.55$ and $0.45$. The arrows in the figure indicate the $\alpha$ relaxation time and the $\beta$ relaxation time, $\tau_\beta$. The $\beta$ relaxation time was determined by finding the first inflection point of $F_s(\vec{k}; t)$ as a function of $\ln[t]$. For $T = 1.0$, this inflection point does not exist. The peak in the ratio $S_4(\vec{k}, \vec{q}_\perp; t)/S_4(\vec{k}, \vec{q}_\parallel; t)$ (i.e. the maximum anisotropy) occurs between the $\beta$ and the $\alpha$ relaxation times, but is closer to the $\beta$ relaxation time for the lower temperatures. However, the correlated motion is still strongly anisotropic around $\tau_\alpha$.

Finally, we compared $S_4(\vec{k}, \vec{q}_0; t)$ for the smallest wavevector allowed due to the periodic boundary conditions, $|\vec{q}_0| = 2\pi/L$, with the four-point susceptibility

$$\chi_4(k; t) = \frac{1}{N} \sum_{n,m} \langle \hat{F}_n(\vec{k}; t) \hat{F}_m(-\vec{k}; t) \rangle - \langle \hat{F}_n(\vec{k}; t) \rangle \langle \hat{F}_m(-\vec{k}; t) \rangle. \qquad (9)$$

As observed before [20], while $S_4(\vec{k}, \vec{q} = 0; t) = \chi_4(k; t)$, the susceptibility $\chi_4(k; t)$ is ensemble dependent, and in a constant-$N$ ensemble $\lim_{\vec{q}\to 0} S_4(\vec{k}, \vec{q}; t) \neq \chi_4(k; t)$. In figure 6 we show the correlation function $S_4(\vec{k}, \vec{q}_0; t)$ and the susceptibility $\chi_4(k; t)$ for several angles $\theta$ between vectors $\vec{q}_0$ and $\vec{k}$ for $T = 1.0$, $0.55$ and $0.45$. For a fixed $\theta$ there is a peak in $S_4(\vec{k}, \vec{q}_0; t)$ around $\tau_\alpha$. The exact position of the peak depends on the angle between $\vec{q}_0$ and $\vec{k}$, and occurs at a time larger than $\tau_\alpha$ for $\vec{q}_0$ parallel to $\vec{k}$, but smaller than the $\tau_\alpha$ for $\vec{q}_0$ perpendicular to $\vec{k}$. It is clear from figure 6 that the time dependence of the correlation function $S_4(\vec{k}, \vec{q}_0; t)$ and that of the susceptibility $\chi_4(k; t)$ are quite different. This is significant because time dependence
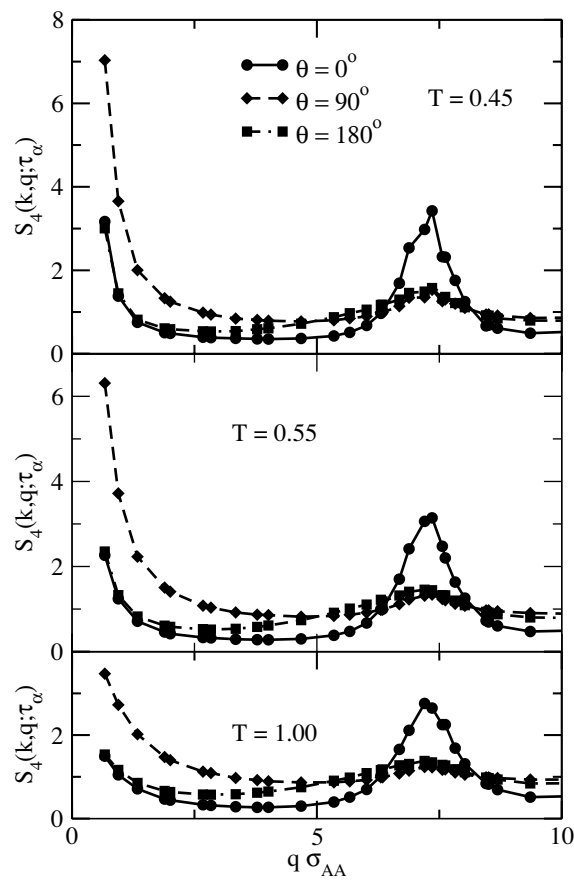
**Figure 4.** The correlation function $S_4(\vec{k}, \vec{q}; \tau_\alpha)$ for $T = 0.45, 0.55$ and $1.0$. The angle $\theta$ is the angle between $\vec{k}$ and $\vec{q}$.
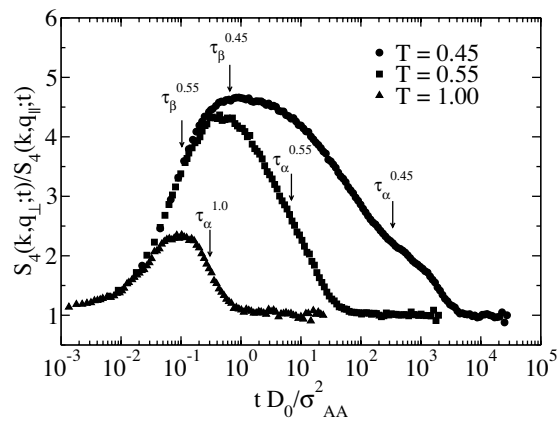


**Figure 5.** The ratio $S_4(\vec{k}, q_\perp; t)/S_4(\vec{k}, q_\parallel; t)$ for $T = 1.0, 0.55$ and $0.45$. The arrows indicate the $\alpha$ and the $\beta$ relaxation times.
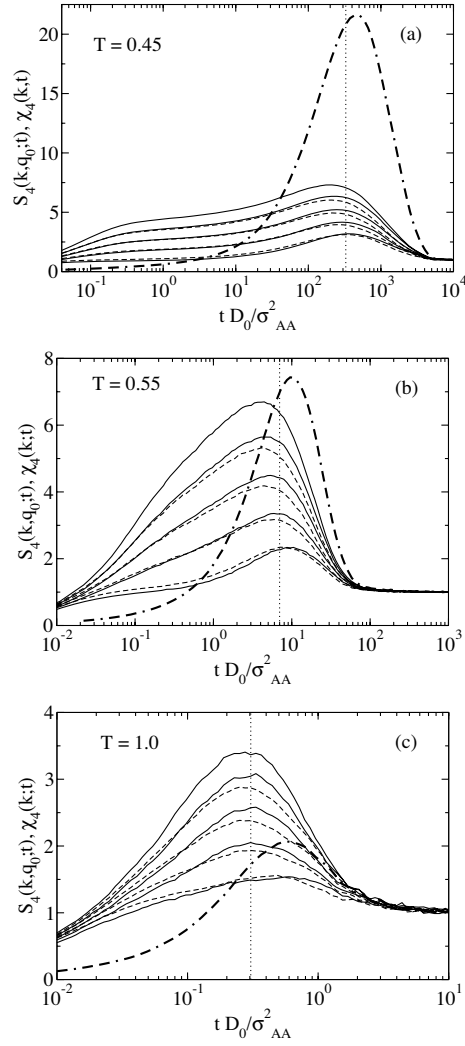
**Figure 6.** The four-point correlation function $S_4(\vec{k}, \vec{q}_0; t)$ as a function of time for $T = 0.45, 0.55$ and 1.0. The solid lines are for the angles 0°, 30°, 45°, 60° and 90° listed from bottom to top. The dashed lines represent the angles 120°, 135°, 150° and 180° listed from top to bottom. The dark dashed dotted line is $\chi_4(k; t)$ and the vertical dotted line marks the $\alpha$ relaxation time.

predicted by recent extensions of the mode-coupling theory [21] for the correlation function $S_4(\vec{k}, \vec{q}; t)$ are usually checked against simulation results for the susceptibility $\chi_4(k; t)$ [9, 22].

## 5. Conclusions

We have shown that there is a pronounced anisotropy of the correlations of the relaxation of particles in a model supercooled liquid even on the timescale of the $\alpha$ relaxation time. The anisotropy of the short-range correlations seems to be weakly temperature dependent. On the other hand, the anisotropy of the long-range correlations, revealed by the four-point structure factor, is more pronounced at low temperatures. This anisotropy will need to be addressed

in theoretical descriptions of heterogeneous dynamics of supercooled liquids. In particular, theoretical input is needed in order to elucidate the relation between anisotropic four-point correlation functions and a dynamic correlation length. Finally, we expect that the anisotropy of the four-point correlation functions examined in this paper will help to differentiate between competing theoretical descriptions of heterogeneous dynamics.

## Acknowledgment

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