# Supplemental Material: Phase Separation in Alkali Silicate Glasses Detected Through Inverse Laplace Transform of <sup>29</sup>Si Nuclear Magnetic Resonance Echo Train Decay

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### S1. Residual heteronuclear dipolar coupling between spin 1/2 and quadrupolar nuclei

Here, we review the theory behind the residual dipolar coupling to a spin 1/2 nucleus from N half-integer quadrupolar nuclei under MAS. In this work, the spin 1/2 nucleus corresponds to the <sup>29</sup>Si nuclide and the quadrupolar nuclei correspond to the <sup>7</sup>Li, <sup>23</sup>Na, <sup>39</sup>K, <sup>133</sup>Cs, and <sup>27</sup>Al nuclides.

We start by writing the first-order Hamiltonian in the rotating frame as

$$\hat{\mathcal{H}}/\hbar = \sum_{k=1}^{N} \left( \underbrace{\omega_{q,k} \frac{R_{2,0}^{\{q,k\}}}{3\zeta_{q,k}} \hat{T}_{2,0}(\mathbf{I}_{k})}_{\text{Quadrupolar}} + \underbrace{-\omega_{0} \left\{ \sigma_{\text{iso,k}} + \zeta_{\sigma,k} \sqrt{\frac{2}{3}} \frac{R_{2,0}^{\{\sigma,k\}}}{\zeta_{\sigma,k}} \right\} \hat{I}_{k,z}}_{\text{Nuclear Shielding}} + \underbrace{\omega_{d,k}^{IS} \sqrt{\frac{2}{3}} \frac{A_{2,0}^{\{d,k\}}}{\zeta_{d,k}^{IS}/2} \hat{S}_{z} \hat{I}_{k,z}}_{\text{Heteronuclear Dipolar}} \right) \\ + \underbrace{\sum_{j \neq k} \omega_{d,kj}^{II} \frac{R_{2,0}^{\{d,k\}}}{\zeta_{d,kj}^{II}/2} \hat{T}_{2,0}(\mathbf{I}_{k},\mathbf{I}_{j}), \quad (1)}_{\text{Homonuclear Dipolar}} \right)$$

where the  $I_k$  represent the half-integer quadrupolar nuclei and S represents the spin 1/2 nucleus. In this Hamiltonian, the interactions, as indicated in the equation above, are the quadrupolar coupling, the nuclear shielding, the heteronuclear dipolar coupling to the spin 1/2 nucleus, and the homonuclear dipolar coupling between the quadrupolar nuclei. See reference 1 for definitions of the individual terms and symbols in this Hamiltonian. For this treatment, we do not need to include the second-order perturbation theory contributions[1] to this Hamiltonian. Of the second-order contributions, the spin 1/2 spectrum is only affected by the cross-term between the heteronuclear dipolar and quadrupolar couplings, which is linear in  $\hat{S}_z$  and readily removed by the  $\pi$ -pulse train. As we show below, it is the homonuclear dipolar coupling that is responsible for creating the residual heteronuclear dipolar couplings that dominate the <sup>29</sup>Si coherence lifetimes in this study.

Preprint submitted to Elsevier

Thus, the first step in understanding the residual heteronuclear dipolar coupling of <sup>29</sup>Si to a quadrupolar nucleus under MAS begins with the strong homonuclear dipolar coupling between the quadrupolar nuclei. Without this term, the Hamiltonian in Eq. (1) is inhomogeneous as defined by Maricq and Waugh[2], i.e., during sample rotation, the Hamiltonian commutes with itself at all times during the rotor period. For an inhomogeneous Hamiltonian, one can show that all the anisotropic interactions, including the heteronuclear dipolar coupling, average to zero under magic-angle spinning. It is the so-called flip-flop term in the strong homonuclear dipolar coupling Hamiltonian, i.e.,

$$\hat{T}_{2,0}(\mathbf{I}_1, \mathbf{I}_2) = \frac{1}{\sqrt{6}} \left[ 3\hat{I}_{1,z}\hat{I}_{2,z} - \mathbf{I}_1 \cdot \mathbf{I}_2 \right] = \frac{1}{\sqrt{6}} \left[ 2\hat{I}_{1,z}\hat{I}_{2,z} - \frac{1}{2} \underbrace{(\hat{I}_{1,+}\hat{I}_{2,-} + \hat{I}_{1,-}\hat{I}_{2,+})}_{\text{flip-flop term}} \right],$$
(2)

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which makes the total Hamiltonian homogeneous, i.e., it does not commute at all times during sample rotation and leads to the residual heteronuclear dipolar coupling to the <sup>29</sup>Si nuclei under MAS.

#### S1.1. Truncation of the Strong Homonuclear Dipolar Coupling by the 1st-order Quadrupolar Coupling

The strong homonuclear couplings between quadrupolar nuclei are partially reduced to weak ones when the quadrupolar nuclei have a strong first-order quadrupolar coupling. That is, the flip-flop terms associated with the satellite transition operators are truncated out of the Hamiltonian. To illustrate this effect, we expand the flip-flop terms,  $\hat{I}_{1,+}\hat{I}_{2,-}$  and  $\hat{I}_{1,-}\hat{I}_{2,+}$ , out in terms of fictitious spin 1/2 operators[3, 4] in the spin I = 3/2 case, where

$$\hat{I}_{z} = 3\hat{I}_{z}^{1-4} + \hat{I}_{z}^{2-3}, \quad \hat{I}_{+} = \sqrt{3}\hat{I}_{+}^{1-2} + \sqrt{3}\hat{I}_{+}^{3-4} + 2\hat{I}_{+}^{2-3}, \quad \text{and} \quad \hat{I}_{-} = \sqrt{3}\hat{I}_{-}^{1-2} + \sqrt{3}\hat{I}_{-}^{3-4} + 2\hat{I}_{-}^{2-3}.$$
(3)

We obtain

$$\hat{I}_{1,+}\hat{I}_{2,-} = \left(\sqrt{3}\hat{I}_{1,+}^{1-2} + \sqrt{3}\hat{I}_{1,+}^{3-4} + 2\hat{I}_{1,+}^{2-3}\right) \left(\sqrt{3}\hat{I}_{2,-}^{1-2} + \sqrt{3}\hat{I}_{2,-}^{3-4} + 2\hat{I}_{2,-}^{2-3}\right) \\
= 3\hat{I}_{1,+}^{1-2}\hat{I}_{2,-}^{1-2} + 3\hat{I}_{1,+}^{1-2}\hat{I}_{2,-}^{3-4} + 2\sqrt{3}\hat{I}_{1,+}^{1-2}\hat{I}_{2,-}^{2-3} + 3\hat{I}_{1,+}^{3-4}\hat{I}_{2,-}^{1-2} + 3\hat{I}_{1,+}^{3-4}\hat{I}_{2,-}^{3-4} + 2\sqrt{3}\hat{I}_{1,+}^{3-4}\hat{I}_{2,-}^{2-3} + 2\sqrt{3}\hat{I}_{1,+}^{2-3}\hat{I}_{2,-}^{2-3} + 2\sqrt{3}\hat{I}_{1,+}^{2-3}\hat{I}_{2,-}^{2-3} + 2\sqrt{3}\hat{I}_{1,+}^{2-3}\hat{I}_{2,-}^{2-3} + 4\hat{I}_{1,+}^{2-3}\hat{I}_{2,-}^{2-3}, \quad (4)$$

and

$$\hat{I}_{1,-}\hat{I}_{2,+} = \left(\sqrt{3}\hat{I}_{1,-}^{1-2} + \sqrt{3}\hat{I}_{1,-}^{3-4} + 2\hat{I}_{1,-}^{2-3}\right) \left(\sqrt{3}\hat{I}_{2,+}^{1-2} + \sqrt{3}\hat{I}_{2,+}^{3-4} + 2\hat{I}_{2,+}^{2-3}\right) \\
= 3\hat{I}_{1,-}^{1-2}\hat{I}_{2,+}^{1-2} + 3\hat{I}_{1,-}^{1-2}\hat{I}_{2,+}^{3-4} + 2\sqrt{3}\hat{I}_{1,-}^{1-2}\hat{I}_{2,+}^{2-3} + 3\hat{I}_{1,-}^{3-4}\hat{I}_{2,+}^{1-2} + 3\hat{I}_{1,-}^{3-4}\hat{I}_{2,+}^{3-4} + 2\sqrt{3}\hat{I}_{1,-}^{3-4}\hat{I}_{2,+}^{2-3} + 2\sqrt{3}\hat{I}_{1,-}^{2-3}\hat{I}_{2,+}^{2-3} + 2\sqrt{3}\hat{I}_{1,-}^{2-3}\hat{I}_{2,+}^{2-3} + 2\sqrt{3}\hat{I}_{1,-}^{2-3}\hat{I}_{2,+}^{2-3} + 2\sqrt{3}\hat{I}_{1,-}^{2-3}\hat{I}_{2,+}^{2-3} + 4\hat{I}_{1,-}^{2-3}\hat{I}_{2,+}^{2-3} \quad (5)$$

One can show, by moving the strong homonuclear dipolar coupling Hamiltonian into the interaction frame of the first-order quadrupolar Hamiltonian, that all the terms involving the satellite transitions undergo fast oscillations and can be truncated away to first-order. Returning to the rotating frame leaves

$$\hat{I}_{1,+}\hat{I}_{2,-} + \hat{I}_{1,-}\hat{I}_{2,+} \approx 4\hat{I}_{1,+}^{2-3}\hat{I}_{2,-}^{2-3} + 4\hat{I}_{1,-}^{2-3}\hat{I}_{2,+}^{2-3}, \tag{6}$$

and

$$\hat{T}_{2,0}(\mathbf{I}_1, \mathbf{I}_2) = \frac{2}{\sqrt{6}} \left( 9\hat{I}_{1,z}^{1-4}\hat{I}_{2,z}^{1-4} + 3\hat{I}_{1,z}^{1-4}\hat{I}_{2,z}^{2-3} + 3\hat{I}_{1,z}^{2-3}\hat{I}_{2,z}^{1-4} + \hat{I}_{1,z}^{2-3}\hat{I}_{2,z}^{2-3} - \hat{I}_{1,+}^{2-3}\hat{I}_{2,-}^{2-3} - \hat{I}_{1,-}^{2-3}\hat{I}_{2,+}^{2-3} \right), \quad (7)$$

Thus, only the flip-flop terms associated with the central transition survive in the presence of a large firstorder quadrupolar coupling. In other words, the homonuclear dipolar couplings involving satellite transitions are weak, while the homonuclear dipolar coupling between central transitions remains strong.

# S1.2. Truncation of flip-flop terms by large shift anisotropy

In the case of <sup>133</sup>Cs, there is also the possibility of large nuclear shielding (or shift) anisotropies, due to the greater number of electrons in the closed shell configuration of the Cesium cation. One can similarly move into the interaction frame of the first-order nuclear shielding Hamiltonian and show that all the flip-flop terms, including the central transition, are eliminated to first-order, making the homonuclear dipolar coupling between all transitions weak. Without any flip-flop terms, the rotating frame Hamiltonian is inhomogeneous, and all anisotropic contributions average to zero under MAS. This mechanism for eliminating residual dipolar couplings can be particularly effective in paramagnetic samples.[5]

# S1.3. Residual Heteronuclear Dipolar Coupling to Quadrupolar Nuclei under MAS

With only a strong homonuclear dipolar coupling between central transitions of the quadrupolar nuclei remaining, we can separate the Hamiltonian into inhomogeneous and homogeneous terms,

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{\text{inhom}} + \hat{\mathcal{H}}_{\text{hom}},\tag{8}$$

depending on whether the term involves the central transition operators of the quadrupolar nuclei.

In the spin 3/2 case, where we have

$$\hat{T}_{2,0}(\mathbf{I}) = \hat{I}_z^{1-2} - \hat{I}_z^{3-4},\tag{9}$$

we obtain

$$\hat{\mathcal{H}}_{\text{inhom}}/\hbar = \sum_{k=1}^{N} \left( \underbrace{\omega_{q,k} \frac{R_{2,0}^{\{q,k\}}}{3\zeta_{q,k}} (\hat{I}_{k,z}^{1-2} - \hat{I}_{k,z}^{3-4})}_{\text{Quadrupolar}} + \underbrace{-\omega_{0} \left\{ \sigma_{\text{iso,k}} + \zeta_{\sigma,k} \sqrt{\frac{2}{3}} \frac{R_{2,0}^{\{\sigma,k\}}}{\zeta_{\sigma,k}} \right\} 3\hat{I}_{k,z}^{1-4} + \underbrace{\omega_{d,k}^{IS} \sqrt{\frac{2}{3}} \frac{A_{2,0}^{\{d,k\}}}{\zeta_{d,k}^{IS}/2}}_{\text{Heteronuclear Dipolar}} \hat{S}_{z} 3\hat{I}_{k,z}^{1-4}} + \underbrace{\sqrt{\frac{2}{3}} \sum_{j \neq k} \omega_{d,kj}^{II} \frac{R_{2,0}^{\{d,kj\}}}{\zeta_{d,kj}^{I}/2} 9\hat{I}_{k,z}^{1-4} \hat{I}_{j,z}^{1-4}}, \quad (10)$$

and

$$\hat{\mathcal{H}}_{\text{hom}}/\hbar = \sum_{k=1}^{N} \left( \underbrace{-\omega_{0} \left\{ \sigma_{\text{iso,k}} + \zeta_{\sigma,k} \sqrt{\frac{2}{3}} \frac{R_{2,0}^{\{\sigma,k\}}}{\zeta_{\sigma,k}} \right\} \hat{I}_{k,z}^{2-3}}_{\text{Nuclear Shielding}} + \underbrace{\omega_{d,k}^{IS} \sqrt{\frac{2}{3}} \frac{A_{2,0}^{\{d,k\}}}{\zeta_{d,k}^{IS}/2} \hat{S}_{z} \hat{I}_{k,z}^{2-3}}_{\text{Heteronuclear Dipolar}} \right) \\
+ \underbrace{\sqrt{\frac{2}{3}} \sum_{j \neq k} \omega_{d,kj}^{II} \frac{R_{2,0}^{\{d,kj\}}}{\zeta_{d,kj}^{II}/2} \left( 3\hat{I}_{k,z}^{1-4} \hat{I}_{j,z}^{2-3} + 3\hat{I}_{k,z}^{2-3} \hat{I}_{j,z}^{1-4} + \hat{I}_{k,z}^{2-3} \hat{I}_{j,z}^{2-3} - \hat{I}_{k,+}^{2-3} \hat{I}_{j,-}^{2-3} - \hat{I}_{k,-}^{2-3} \hat{I}_{j,+}^{2-3}} \right)}_{\text{Homonuclear Dipolar}}. (11)$$

Under MAS, the Hamiltonian becomes time-dependent,

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_{inhom}(t) + \hat{\mathcal{H}}_{hom}(t).$$
(12)

Using an Average Hamiltonian Theory (AHT) expansion[2], all the anisotropic terms are eliminated in the zeroth-order term,

$$H^{(0)} = \frac{1}{t_R} \int_0^{t_R} \hat{\mathcal{H}}(t) dt = -\sum_k \omega_0 \sigma_{\mathrm{iso,k}} \hat{I}_{k,z}, \qquad (13)$$

and the leading anisotropic term appears at the next order,

$$H^{(1)} = -\frac{i}{2t_R} \int_0^{t_R} dt_2 \int_{t_1}^{t_R} dt_1 \left[ \hat{\mathcal{H}}(t_2), \hat{\mathcal{H}}(t_1) \right].$$
(14)

Since

$$[\hat{\mathcal{H}}_{inhom}(t_2), \hat{\mathcal{H}}_{inhom}(t_1)] = 0, \text{ and } [\hat{\mathcal{H}}_{inhom}(t_2), \hat{\mathcal{H}}_{hom}(t_1)] = 0,$$
(15)

and

$$[\hat{\mathcal{H}}_{\text{hom}}(t_2), \hat{\mathcal{H}}_{\text{hom}}(t_1)] \neq 0,$$
(16)

the leading term in an Average Hamiltonian Theory (AHT) expansion[2] are the cross-terms of the homonuclear dipolar coupling with the heteronuclear dipolar coupling—and also the nuclear shielding terms,

$$H^{(1)} = -\frac{i}{2t_R} \int_0^{t_R} dt_2 \int_0^{t_2} dt_1 \left[ \hat{\mathcal{H}}_{\text{hom}}(t_2), \hat{\mathcal{H}}_{\text{hom}}(t_1) \right].$$
(17)

For convenience we define

$$\hat{\mathcal{H}}_{\text{hom}}(t) = \hat{A}(t) + \hat{B}(t), \qquad (18)$$

where

$$\hat{A}(t) = \omega_{d,k}^{IS} \sqrt{\frac{2}{3}} \frac{A_{2,0}^{\{d,k\}}(t)}{\zeta_{d,k}^{IS}/2} \hat{S}_z \, \hat{I}_{k,z}^{2-3} = a(t) \hat{I}_{k,z}^{2-3},\tag{19}$$

and

$$\hat{B}(t) = \sqrt{\frac{2}{3}} \sum_{j \neq k} \omega_{d,kj}^{II} \frac{R_{2,0}^{\{d,kj\}}(t)}{\zeta_{d,kj}^{II}/2} \left( 3\hat{I}_{k,z}^{1-4}\hat{I}_{j,z}^{2-3} + 3\hat{I}_{k,z}^{2-3}\hat{I}_{j,z}^{1-4} + \hat{I}_{k,z}^{2-3}\hat{I}_{j,z}^{2-3} - \hat{I}_{k,+}^{2-3}\hat{I}_{j,-}^{2-3} - \hat{I}_{k,-}^{2-3}\hat{I}_{j,+}^{2-3} \right) \\ = b(t) \left( 3\hat{I}_{k,z}^{1-4}\hat{I}_{j,z}^{2-3} + 3\hat{I}_{k,z}^{2-3}\hat{I}_{j,z}^{1-4} + \hat{I}_{k,z}^{2-3}\hat{I}_{j,z}^{2-3} - \hat{I}_{k,+}^{2-3}\hat{I}_{j,-}^{2-3} - \hat{I}_{k,-}^{2-3}\hat{I}_{j,+}^{2-3} \right).$$
(20)

The AHT term becomes

$$H^{(1)} = -\frac{i}{2t_R} \int_0^{t_R} dt_2 \int_0^{t_2} dt_1 \left[ \hat{A}(t_2) + \hat{B}(t_2), \hat{A}(t_1) + \hat{B}(t_1) \right],$$
  
$$= -\frac{i}{2t_R} \int_0^{t_R} dt_2 \int_0^{t_2} dt_1 \left( \left[ \hat{A}(t_2), \hat{B}(t_1) \right] + \left[ \hat{B}(t_2), \hat{A}(t_1) \right] + \left[ \hat{B}(t_2), \hat{B}(t_1) \right] \right). \quad (21)$$

We can ignore the  $[\hat{B}(t_2), \hat{B}(t_1)]$  term since this will not affect the <sup>29</sup>Si spectrum. Recalling that  $[\hat{I}_z, \hat{I}_{\pm}] = \pm \hat{I}_{\pm}$ , we obtain

$$[\hat{A}(t_2), \hat{B}(t_1)] = a(t_2)b(t_1) \left[ \hat{I}_{k,z}^{2-3}, -\hat{I}_{k,+}^{2-3}\hat{I}_{j,-}^{2-3} - \hat{I}_{k,-}^{2-3}\hat{I}_{j,+}^{2-3} \right]$$

$$= -a(t_2)b(t_1) \left[ \hat{I}_{k,z}^{2-3}, \hat{I}_{k,+}^{2-3} \right] \hat{I}_{j,-}^{2-3} - a(t_2)b(t_1) \left[ \hat{I}_{k,z}^{2-3}, \hat{I}_{k,-}^{2-3} \right] \hat{I}_{j,+}^{2-3}$$

$$= a(t_2)b(t_1) \left( \hat{I}_{k,-}^{2-3}\hat{I}_{j,+}^{2-3} - \hat{I}_{k,+}^{2-3}\hat{I}_{j,-}^{2-3} \right),$$

$$(22)$$

 $\quad \text{and} \quad$ 

$$\left[\hat{B}(t_2), \hat{A}(t_1)\right] = a(t_1)b(t_2) \left[-\hat{I}_{k,+}^{2-3}\hat{I}_{j,-}^{2-3} - \hat{I}_{k,-}^{2-3}\hat{I}_{j,+}^{2-3}, \hat{I}_{k,z}^{2-3}\right] = -a(t_1)b(t_2) \left(\hat{I}_{k,-}^{2-3}\hat{I}_{j,+}^{2-3} - \hat{I}_{k,+}^{2-3}\hat{I}_{j,-}^{2-3}\right), \quad (23)$$

which bring us to

$$H^{(1)} = -\frac{i}{2t_R} \left( \hat{I}_{k,-}^{2-3} \hat{I}_{j,+}^{2-3} - \hat{I}_{k,+}^{2-3} \hat{I}_{j,-}^{2-3} \right) \int_0^{t_R} dt_2 \int_0^{t_2} dt_1 \left( a(t_2)b(t_1) - a(t_1)b(t_2) \right).$$
(24)

Substituting back for a(t) and b(t) gives

$$a(t_2)b(t_1) = \hat{S}_z \frac{2}{3} \sum_{j \neq k} \omega_{d,kj}^{II} \omega_{d,k}^{IS} \frac{R_{2,0}^{\{d,kj\}}(t_1)}{\zeta_{d,kj}^{II}/2} \frac{A_{2,0}^{\{d,k\}}(t_2)}{\zeta_{d,k}^{IS}/2}.$$
(25)

Recalling that

$$R_{L,0}(t) = \sum_{m=-L}^{L} \mathcal{D}_{m,0}^{(L)}(\omega_R t, \theta_R, 0) R'_{L,m} = \sum_{m=-L}^{L} e^{-im\omega_R t} d_{m,0}^{(L)}(\theta_R) R'_{L,m},$$
(26)

we obtain

$$a(t_{2})b(t_{1}) = \hat{S}_{z}\frac{2}{3}\sum_{j\neq k}\omega_{d,kj}^{II}\omega_{d,k}^{IS}\sum_{m\neq 0}\sum_{n\neq 0}\frac{R'_{2,m}}{\zeta_{d,kj}^{II}/2}\frac{A'_{2,n}}{\zeta_{d,k}^{IS}/2}d_{m,0}^{(2)}(\theta_{R})d_{n,0}^{(2)}(\theta_{R})e^{-i\omega_{R}(mt_{1}+nt_{2})},$$

$$=\sum_{m\neq 0}\sum_{n\neq 0}\hat{C}_{m,n}e^{-i\omega_{R}(mt_{1}+nt_{2})}.$$
(27)

Similarly, we obtain

$$a(t_1)b(t_2) = \hat{S}_z \frac{2}{3} \sum_{j \neq k} \omega_{d,kj}^{II} \omega_{d,k}^{IS} \sum_{m \neq 0} \sum_{n \neq 0} \frac{R'_{2,m}}{\zeta_{d,kj}^{II}/2} \frac{A'_{2,n}}{\zeta_{d,k}^{IS}/2} d_{m,0}^{(2)}(\theta_R) d_{n,0}^{(2)}(\theta_R) e^{-i\omega_R(mt_2+nt_1)},$$

$$= \sum_{m \neq 0} \sum_{n \neq 0} \hat{C}_{m,n} e^{-i\omega_R(mt_2+nt_1)},$$
(28)

where

$$\hat{C}_{m,n} = \hat{S}_z \frac{2}{3} \sum_{j \neq k} \omega_{d,kj}^{II} \omega_{d,kj}^{IS} \frac{R'_{2,m}}{\zeta_{d,kj}^{II}/2} \frac{A'_{2,n}}{\zeta_{d,k}^{IS}/2} d_{m,0}^{(2)}(\theta_R) d_{n,0}^{(2)}(\theta_R).$$
<sup>(29)</sup>

Since  $d_{0,0}^{(2)}(\theta_R) = 0$ , we eliminate the m = n = 0 terms in the two summations. Focusing on the integrals, we find

$$\int_{0}^{t_{R}} dt_{2} e^{-in\omega_{R}t_{2}} \int_{0}^{t_{2}} dt_{1} e^{-im\omega_{R}t_{1}} = \int_{0}^{t_{R}} dt_{2} e^{-in\omega_{R}t_{2}} \left(\frac{1 - e^{-im\omega_{R}t_{2}}}{im\omega_{R}}\right)$$
(30)

$$\frac{1}{im\omega_R} \int_0^{t_R} dt_2 \, e^{-in\omega_R t_2} - \frac{1}{im\omega_R} \int_0^{t_R} dt_2 \, e^{-i(m+n)\omega_R t_2}.$$
 (31)

Since  $n \neq 0$  and  $m \neq 0$ , the first integral goes to zero, and the second integral is non-zero only when m = -n, and evaluates to

=

$$\int_{0}^{t_{R}} dt_{2} e^{-in\omega_{R}t_{2}} \int_{0}^{t_{2}} dt_{1} e^{-im\omega_{R}t_{1}} = -\frac{t_{R}}{im\omega_{R}}.$$
(32)

Similarly, the other double integral is non-zero when m = -n giving

$$\int_{0}^{t_{R}} dt_{2} e^{-im\omega_{R}t_{2}} \int_{0}^{t_{2}} dt_{1} e^{-in\omega_{R}t_{1}} = -\frac{t_{R}}{in\omega_{R}} = \frac{t_{R}}{im\omega_{R}}.$$
(33)

Subtracting the two double integrals gives

$$\int_{0}^{t_{R}} dt_{2} e^{-in\omega_{R}t_{2}} \int_{0}^{t_{2}} dt_{1} e^{-im\omega_{R}t_{1}} - \int_{0}^{t_{R}} dt_{2} e^{-im\omega_{R}t_{2}} \int_{0}^{t_{2}} dt_{1} e^{-in\omega_{R}t_{1}} = -\frac{2t_{R}}{im\omega_{R}},$$
(34)

giving us

$$H^{(1)} = \frac{1}{\omega_R} \sum_{m \neq 0} \frac{\hat{C}_{m,-m}}{m} \left( \hat{I}_{k,-}^{2-3} \hat{I}_{j,+}^{2-3} - \hat{I}_{k,+}^{2-3} \hat{I}_{j,-}^{2-3} \right),$$
(35)

which expands to

$$H^{(1)} = \sum_{j \neq k} \frac{\omega_{d,kj}^{II} \omega_{d,k}^{IS}}{\omega_R} \left( \sum_{m \neq 0} \frac{2}{3m} \frac{R'_{2,m}}{\zeta_{d,kj}^{II}/2} \frac{A'_{2,-m}}{\zeta_{d,kj}^{IS}/2} d^{(2)}_{m,0}(\theta_R) d^{(2)}_{-m,0}(\theta_R) \right) \left( \hat{I}_{k,-}^{2-3} \hat{I}_{j,+}^{2-3} - \hat{I}_{k,+}^{2-3} \hat{I}_{j,-}^{2-3} \right) \hat{S}_z.$$
(36)

Not only are the weak homonuclear dipolar coupling terms involving the satellite transition completely removed under MAS, but also the parts of the heteronuclear dipolar coupling involving the satellite transition. Most importantly, the parts of the heteronuclear dipolar coupling involving the central transition operators are partially removed with MAS, with the residual heteronuclear dipolar coupling line width coming from the central transition cross-terms with the homonuclear dipolar coupling. It is these cross-terms that dominate the echo-train decay, which is proportional to

$$\frac{\omega_d^{II}\omega_d^{IS}}{\omega_R} = \frac{1}{\omega_R} \cdot \left(\frac{\mu_0}{4\pi}\right)^2 \cdot \frac{\gamma_I^2\hbar}{r_{II}^3} \cdot \frac{\gamma_I\gamma_S\hbar}{r_{IS}^3}.$$
(37)

Thus, the key factors to consider when interpreting the variations in the <sup>29</sup>Si coherence lifetime distributions in the alkali silicate glasses are the size of the gyromagnetic ratio for the quadrupolar nuclei of the alkali cation, the distance between alkali cations, and the distance between the alkali cations and the <sup>29</sup>Si nuclides. This is why the <sup>29</sup>Si coherence lifetimes are particularly sensitive to phase separation since the stronger homonuclear dipolar couplings between alkali nuclides in the alkali-rich phases "amplify" the heteronuclear dipolar coupling to <sup>29</sup>Si in this cross term.

#### S1.4. Finite $\pi$ -pulse effects

The combined effect of MAS and a  $\pi$ -pulse train can be analyzed using a second averaging approach.[6] In this approach, the first average is calculated over the shorter rotor period, and the second average is calculated over the longer  $\pi$ -pulse period. While the residual dipolar coupling averages to zero in a simple AHT treatment that assumes infinitely short  $\pi$  pulses, an AHT treatment using finite length  $\pi$ -pulses shows that some residual dipolar coupling terms remain.[7]

# S2. Chemical Shift Mode Analysis

Chemical shift modes for  $Q^3$  and  $Q^4$  sites were determined from a least-squares analysis of the isotropic 1D MAS spectrum, obtained from the Fourier transform of the first collected echo of each measurement, to the function

$$S(\Omega) = A_3 \exp\left(\frac{1}{2} \frac{(\overline{\Omega}_3 - \Omega)^2}{\sigma_3^2}\right) + A_4 \exp\left(\frac{1}{2} \frac{(\overline{\Omega}_4 - \Omega)^2}{\sigma_4^2}\right),\tag{38}$$

where  $\overline{\Omega}_n$  is the mean position,  $\sigma_n$  is the standard deviation, and  $A_n$  is the amplitude for the  $\mathbb{Q}^n$  resonance. The solid black lines and grey dashed lines shown in Figure 2 represent the experimental spectrum and the best fit to this function. The best-fit parameters are given in Table S1. An accurate ratio of  $\mathbb{Q}^3$  to  $\mathbb{Q}^4$  site populations cannot be gained from this analysis because of differential echo train lifetimes.

	$Q^4$			$Q^3$			$R^2$
Dataset	$\overline{\Omega}_4 \ / \mathrm{ppm}$	$\sigma_4 \ / \mathrm{ppm}$	$A_4$	$\overline{\Omega}_3$ /ppm	$\sigma_3 \ / { m ppm}$	$A_3$	
5Li:95Si	-110.9	4.509	61830	-93.2	7.170	24760	0.93
10Li:90Si	-110.9	4.453	41120	-92.4	6.834	39350	0.91
7Li:2Al:91Si	-110.7	4.312	71140	-99.3	8.712	38870	0.96
5Na:95Si	-110.3	4.629	88680	-93.9	5.050	36810	0.96
5K:95Si	-110.3	4.544	78870	-97.5	3.857	21850	0.95
5Cs: $95$ Si	-110.1	4.450	76150	-99.4	3.206	21570	0.94
10Cs:90Si	-108.9	4.390	86000	-98.6	3.932	53930	0.96
7Cs:2Al:91Si	-108.2	5.273	66700	-98.4	3.471	23770	0.94

Table S1: Best-fit parameters obtained from a least-squares analysis of the experimental 1D MAS spectra of the first echo of each sample to the sum of two Gaussian functions that represent the  $Q^3$  and  $Q^4$  sites. Here,  $\overline{\Omega}_n$  is the mean position,  $\sigma_n$  is the standard deviation, and  $A_n$  is the amplitude for the  $Q^n$  resonance.

Dataset	$\sigma_{ m noise}$	β	r	$\sigma_{\rm residuals}$
5Li:95Si	1110.521	0.11602	18	1526
10Li:90Si	1109.108	0.03808	18	1174
7Li:2Al:91Si	1194.356	0.03808	15	1299
5Na:95Si	1089.445	0.03808	18	1246
5K:95Si	1085.251	0.08003	18	1290
5Cs:95Si	1407.443	0.01250	18	1252
10 Cs: 90 Si	1270.825	0.03808	14	1228
7Cs:2Al:91Si	1163.954	0.03808	14	1312

Table S2: Inverse Laplace parameters. Here,  $\sigma_{\text{noise}}$  is the standard deviation of the noise in the datasets,  $\beta$  is the hyperparameter that promotes sparsity in the solution, r is the truncation index, and  $\sigma_{\text{residuals}}$  are the dataset residuals after the fit. All inversions performed using  $n_{\lambda^{-1}} = 32$  with a super sampling of 20. The hyperparameter  $\beta$  was determined using 5-fold cross-validation.



Figure S1: Photographs of the 5Na:95Si, 5Li:99Si, and 10Li:90Si glasses. The 10Li:90Si glass exhibits strong opalescence, indicating a phase separation that forms spatial domains on the order of 200 nm or higher. All other glasses in this study exhibit no opalescence, consistent with any phase separation occurring below an optical wavelength limit of  $\sim 200$  nm.



S10

Figure S2: X-ray diffraction of the (A) 5Li:95Si and (B) 10Li:90Si glass samples. The 10Li:90Si composition in (B) shows signs of cristobalite crystallization.

#### References

- P. J. Grandinetti, J. T. Ash, and N. M. Trease. Symmetry pathways in solid-state NMR. Prog. Nucl. Mag. Res. Sp., 59:121–196, 2011.
- [2] M. M. Maricq and J. S. Waugh. NMR in rotating solids. J. Chem. Phys., 70:3300, 1979.
- [3] A. Wokaun and R. R. Ernst. Selective excitation and detection in multilevel spin systems: Application of single transition operators. J. Chem. Phys., 67:1752–1758, 1977.
- [4] S. Vega. Fictitious spin-1/2 operator formalism for multiple quantum NMR. J. Chem. Phys., 68:5518– 5527, 1978.
- [5] Y. Ishii, N. P. Wickramasinghe, and S. Chimon. A new approach in 1D and 2D C-13 high-resolution solidstate NMR spectroscopy of paramagnetic organometallic complexes by very fast magic-angle spinning. J. Am. Chem. Soc., 125:3438–3439, 2003.
- [6] M. Mehring. High Resolution NMR Spectroscopy in Solids, volume 11. Springer-Verlag, Berlin, 1983.
- [7] Dale Li, Yanqun Dong, R. G. Ramos, J. D. Murray, K. MacLean, A. E. Dementyev, and S. E. Barrett. Intrinsic origin of spin echoes in dipolar solids generated by strong. *Phys. Rev. B*, 77, 2008.