

Polarized Raman spectroscopic study on the solvent state of glassy LiCl aqueous solutions and the state of relaxed high-density amorphous ices

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(Received 17 March 2011; accepted 3 June 2011; published online 29 June 2011)

We measure polarized OH-stretching Raman spectra of the glassy lithium chloride aqueous solutions (LiCl_{aq} solutions) and the relaxed high-density amorphous ices (HDA). The totally OH symmetric vibrational mode around 3100 cm⁻¹ (*g*₁ mode) for the glassy LiCl_{aq} solutions of 14.3 mol% and the *g*₁ mode for the glassy LiCl_{aq} solution of 10.0 mol% seem to be similar to the *g*₁ mode for HDA at high pressure and the *g*₁ mode for HDA at 1 atm, respectively. This indicates that the solvent state of glassy LiCl_{aq} solution relates to the state of HDA and that the attenuation of the salt effect on water is equivalent to the attenuation of the pressure effect on water. This suggests a possibility that the hydration in electrolyte aqueous solution may relate to high-density liquid water. © 2011 American Institute of Physics. [doi:10.1063/1.3603965]

I. INTRODUCTION

Recent studies of liquid water support a water polymorphism notion that distinct two waters, low-density and high-density liquid (LDL and HDL), exist in a super-cooled region.¹⁻³ If a liquid-liquid critical point (LLCP) relating to LDL and HDL exists, it is expected that the large fluctuation generated at the LLCP should exert an influence not only on properties of liquid pure water but also on structure and function of aqueous solutions. Therefore, the study of the effect of water polymorphism on aqueous solutions should be important for the understanding of the static and dynamic structure of hydrophilic/hydrophobic hydration.

Recently, the several interesting computer simulation studies relating to the applications of water polymorphism on aqueous solutions have been reported.⁴⁻⁸ However, there are few experimental studies relating the applications of water polymorphism on aqueous solutions.⁹⁻¹⁴ The reason is that the direct observation of liquid water at low temperatures is difficult because of rapid crystallization. Reluctantly, we have attempted to understand the water polymorphism from the experimental information of low-density and high-density amorphous ices (LDA and HDA) which correspond to LDL and HDL, respectively. In order to unveil the structures of LDA and HDA, many experimental works have been carried out¹⁵⁻²¹ and it has been found that the structure of LDA differs distinctly from that of HDA. However, it is difficult to apply these experimental results to aqueous solution systems practically. The reasons are that the observations of amorphous ices are carried out always under a non-equilibrium condition.²²⁻²⁵ In addition, a spectrum detected from glassy materials has a broad and vague profile generally and its vagueness makes it difficult to separate only LDA/HDA component distinctly from a spectrum detected from aqueous solution system.

In previous polarized Raman spectroscopic studies of HDA,²³ we have examined the homogeneously disordered

molecular configurations in the HDA relaxed under high pressure and at 1 atm. We have shown that the state of the relaxed HDA is under nearly equilibrium and relates closely to a liquid state. In the present study, we measure the polarized Raman spectra of glassy lithium chloride aqueous solutions (LiCl_{aq} solutions), examine the solvent state of glassy LiCl_{aq} solutions, and compare the state with the state of the relaxed HDA. We will discuss about the similarity between the effect of salts on the solvent water and the effect of pressure on HDA.

II. SAMPLE AND EXPERIMENTAL METHOD

The LiCl_{aq} solutions in the concentration range between 10.0 and 25.0 mol% (*R* = 9 – 3) are vitrified by cooling to 77 K at 1 atm. In this paper, we use conveniently an expression of “mol%” and an expression of “*R*” together, where *R* stands for the number of water moles per mole of salt. When LiCl_{aq} solution above ~10.0 mol% (*R* < ~9) is quenched at a cooling rate of ~5 K/s, it becomes homogeneous glass easily without crystallization.²⁶ We know that when the LiCl_{aq} solution below ~10.0 mol% (*R* > ~9) is cooled at ~5 K/s, the part of solvent water in the LiCl_{aq} solution crystallizes and a mixture of ice *I*_h and LiCl-rich glassy solution is formed.

In order to make the relaxed HDA,²³ first of all, the un-relaxed HDA sample is made by the pressure-induced amorphization of crystalline ice *I*_h at 77 K. In this un-relaxed HDA sample, the inhomogeneously disordered molecular configurations are formed because of the preparation under a non-equilibrium condition. Next, we heat the un-relaxed HDA under 1.5 GPa from 77 to 160 K at 0.3 K/s, keep it at 160 K at 1.5 GPa for 10 min, cool it down to 77 K at 1.5 GPa, and decompress it at 1 atm at 77 K. In this paper, this HDA heated under 1.5 GPa is referred to as “HP-relaxed HDA”. In order to make HDA relaxed at 1 atm, we heat the HP-relaxed HDA to 110 K at 1 atm and cool it to 77 K at 1 atm. This HDA heated at 1 atm is referred to as “1 atm-relaxed HDA”.

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We consider that the inhomogeneously disordered molecular configuration frozen in the un-relaxed HDA is rearranged by annealing and the state of the relaxed HDA is under nearly equilibrium conditions.^{23,24}

The polarized Raman spectra in the OH-stretching vibration range from 2800 to 3800 cm^{-1} are measured by using microscope Raman spectroscopy (Jovin Yvon T-64000). The resolution of the Raman spectrum is about 0.1 cm^{-1} . The incident laser is argon ion laser with wave length of 488.0 nm and power of 500 mW at the source. The intensity of the Raman scattered radiation polarized parallel to the incident light, I_{VV} , and the intensity of the Raman scattered radiation polarized perpendicular to the incident light, I_{VH} , are measured separately. The scattered volume of the HDA sample is almost the same.

The I_{VV} and I_{VH} are corrected for polarized filter and back ground by the instrumental function, and then are converted into the imaginary part of dynamical susceptibility (reduced Raman spectrum), $\chi''(\nu)$,²³ where ν stands for the absolute frequency of the Raman-shifted radiation, written in cm^{-1} . In order to discuss the OH-stretching vibrational Raman spectra quantitatively, the reduced Raman spectra are analyzed by a linear combination of three or four Gaussian functions, $g(\nu)$, as the follows:

$$\chi''(\nu) = \sum_{n=1}^{3 \text{ or } 4} g_n(\nu) = \sum_{n=1}^{3 \text{ or } 4} A_n \exp\left(\frac{-(\nu - \nu_n)^2}{\sigma_n^2}\right),$$

where A_n is the amplitude, ν_n is the central frequency, and σ_n is the distribution. The glassy LiClaq solutions and the relaxed HDA samples are placed in a cryostat and the Raman spectra are recorded at 35 K at 1 atm.

III. RESULTS AND DISCUSSION

$\chi''_{VV}(\nu)$ and $\chi''_{VH}(\nu)$ of glassy LiClaq solutions with various concentrations are shown in Figs. 1 and 2, respectively. It is found that the lowest mode around 3100–3200 cm^{-1} , g_1 mode, in $\chi''_{VH}(\nu)$ is extremely smaller than the g_1 mode in $\chi''_{VV}(\nu)$. Generally, the g_1 mode for H_2O is indentified as a totally symmetric OH-stretching vibration mode.²⁷ In the case of the liquid state, the g_1 mode in $\chi''_{VH}(\nu)$ is extremely smaller than that in $\chi''_{VV}(\nu)$ because of a preservation of the symmetry of vibration caused by the homogeneously disordered molecular configuration.²⁸ Therefore, the remarkably small g_1 modes in $\chi''_{VH}(\nu)$ for the glassy LiClaq solutions indicate that the glassy LiClaq solutions are homogeneously disordered and that no crystalline ices are formed in the samples.

In the present study, we pay attention to only the g_1 mode in $\chi''_{VV}(\nu)$. Generally, it is difficult to decompose the OH-stretching Raman spectrum around 2800–3800 cm^{-1} into several modes because the modes overlap each other. However, we are able to identify the g_1 mode from $\chi''_{VV}(\nu)$ relatively easily because of the reduction of the g_1 mode in $\chi''_{VH}(\nu)$. In addition, we know another advantage that the g_1 mode in $\chi''_{VV}(\nu)$ is highly sensitive to the change in the molecular configuration of hydrogen-bonded networks. Some examples are that, when the liquid water crystallizes to hexagonal ice in

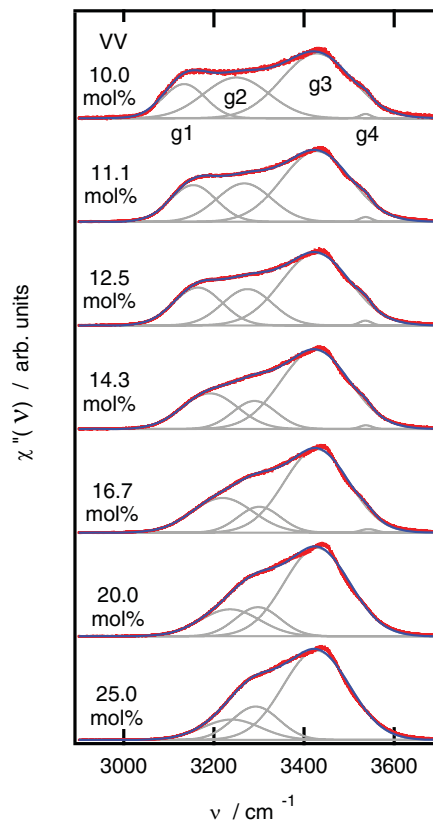


FIG. 1. Polarized (VV) reduced Raman spectra for glassy LiClaq solutions in the OH-stretching region. Solute concentration ranges from 10.0 to 25.0 mol% ($9 > R > 3$). Red dots denote the measured Raman spectra. Blue line denotes results analyzed by a linear combination of four Gaussian functions (gray lines).

which ideal tetrahedral molecular configuration are formed, the broad and weak Raman profile of g_1 mode for liquid water changes drastically to the sharp and strong Raman profile.²⁹ We also know that the g_1 modes of other high-pressure crystalline ices are also sharp as well as the g_1 mode of ice I_h .³⁰ Moreover, it has been reported that the temperature dependence of the g_1 mode for super-cooled liquid water is large.³¹ Namely, the g_1 mode relates strongly to the tetrahedral molecular configuration of hydrogen-bonded network. Here, we aware that the information derived from the analysis of g_1 mode relates to a macroscopic “state” of hydrogen-bonded molecular configuration and not to a microscopic “structure” of hydrogen-bonded molecular configuration. Therefore, in order to examine the state of solvent water in glassy LiClaq solutions, we probe a change of g_1 mode in $\chi''_{VV}(\nu)$ for the glassy LiClaq solutions with the change of concentration.

Unfortunately, the relation between the other modes except g_1 mode and the molecule configurations is not understood well. Additionally, since the higher frequency edge of the g_2 mode overlaps considerably with the g_3 and g_4 modes, it is difficult to extract the g_2 mode efficiently from $\chi''_{VV}(\nu)$. Therefore, we do not discuss qualitatively about these modes in this study. We expect their further studies in future.

The concentration dependence of ν_n for $\chi''_{VV}(\nu)$ is shown in Fig. 3. The ν_1 increases continuously as the concentration increases up to ~ 15 mol% ($R > \sim 5.5$). The ν_1 of

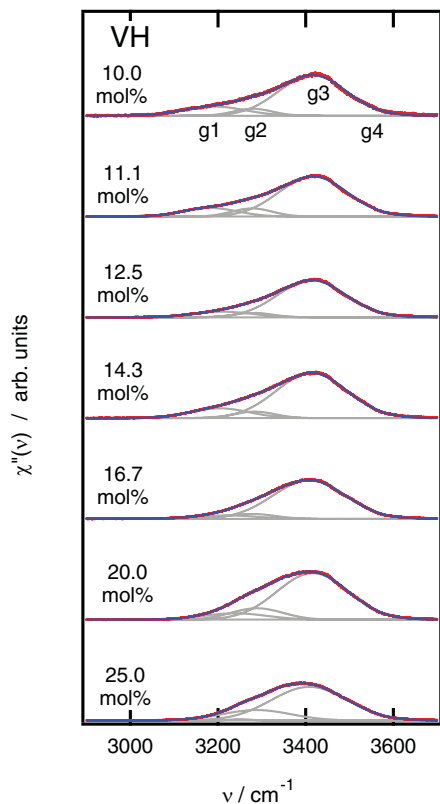


FIG. 2. Depolarized (VH) reduced Raman spectra for glassy LiClq solution in the OH-stretching region. Solute concentration ranges from 10.0 to 25.0 mol% ($9 > R > 3$). Red dots denote the measured Raman spectra. Blue line denotes results analyzed by a linear combination of four Gaussian functions (gray lines).

glassy LiClq solution above ~ 15 mol% ($R < \sim 5.5$) is almost constant.

The concentration dependence of σ_n and the concentration dependence of a ratio of A_n ($\alpha_n = A_n/\sum A_n$) in $\chi''_{VV}(\nu)$ are shown in Figs. 4 and 5, respectively. The σ_1 increases continuously as the concentration increases to ~ 15 mol% ($R > \sim 5.5$). The σ_1 for glassy LiClq solutions above ~ 15 mol% ($R < \sim 5.5$) is almost constant. The α_1 for glassy LiClq solutions below ~ 15 mol% ($R > \sim 5.5$) is almost constant ($\sim 24\%$). As the concentration increases from 16.7 to 25.0 mol%, the α_1 decreases continuously from 24% to 15%.

The concentration dependences of three parameters for the g_1 mode suggest that the solvent state in glassy LiClq solutions below ~ 15 mol% ($R > \sim 5.5$) is different from the solvent state of the glassy solution above ~ 15 mol% ($R < \sim 5.5$). The solvent water in the glassy LiClq solution in the concentration range from ~ 10.0 to ~ 14.3 mol% ($\sim 9 > R > \sim 6$) consists in the first hydration shell and the excess water beyond the first hydration shell,²⁶ is little affected by the salt.³² Therefore, we consider that the change of the g_1 mode in the concentration range from ~ 10.0 to ~ 15 mol% ($\sim 9 > R > \sim 5.5$) may be induced by the change in the glassy state of excess water beyond the first hydration shell. We infer that the contribution of the first hydration shell to the g_1 mode is small because the degree of tetrahedral arrangement is low in the molecular configuration of the first hydration shell.

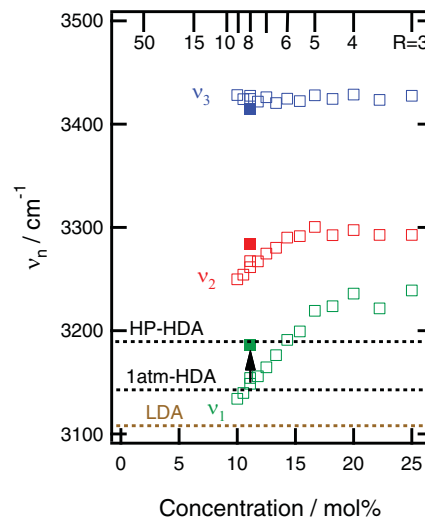


FIG. 3. Concentration dependences of ν_1 , ν_2 , and ν_3 in $\chi''_{VV}(\nu)$. The ν_1 , ν_2 , and ν_3 are presented by green opened square, red opened square, and blue opened square, respectively. Values of ν_1 for the 1 atm-relaxed HDA and the HP-relaxed HDA are presented by black dot lines. Value of ν_1 for the LDA is presented by a brown dot line. The ν_1 , ν_2 , and ν_3 of the densified glassy LiClq solution (11.1 mol%; $R = 8$) are presented by green closed square, red closed square, and blue closed square, respectively. The concentration dependence of ν_4 is not shown in this figure.

Now, we compare the ν_1 of the glassy LiClq solutions with the ν_1 of the relaxed HDAs. The $\chi''_{VV}(\nu)$ of the HP-relaxed HDA and the 1 atm-relaxed HDA are shown in Fig. 6, and their ν_1 are presented in Fig. 3. The ν_1 of the HP-relaxed HDA is 3189 cm^{-1} and it agrees approximately with the ν_1 for the glassy LiClq solution of 14.3 mol% ($R = 6$). On the other hand, the ν_1 of the 1 atm-relaxed HDA is 3142 cm^{-1} and it is similar to the ν_1 of the glassy LiClq solution of 10.0 mol% ($R = 9$). However, the ν_1 of LDA ($\sim 3105 \text{ cm}^{-1}$) (Ref. 23) is much lower than those of all the glassy LiClq solutions measured in this study. These comparisons suggest

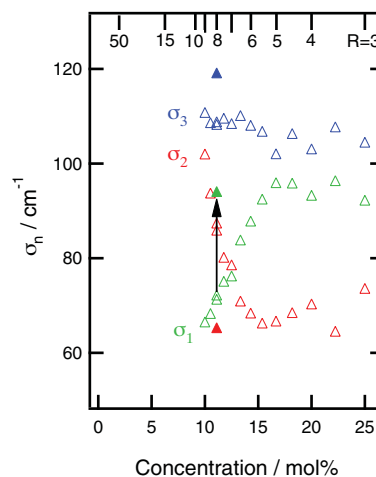


FIG. 4. Concentration dependences of σ_1 , σ_2 , and σ_3 in $\chi''_{VV}(\nu)$. The σ_1 , σ_2 , and σ_3 are presented by green opened triangle, red opened triangle, and blue opened triangle, respectively. The concentration dependence of σ_4 is not shown in this figure. The σ_1 , σ_2 , and σ_3 of the densified glassy LiClq solution (11.1 mol%; $R = 8$) are presented by green closed triangle, red closed triangle, and blue closed triangle, respectively.

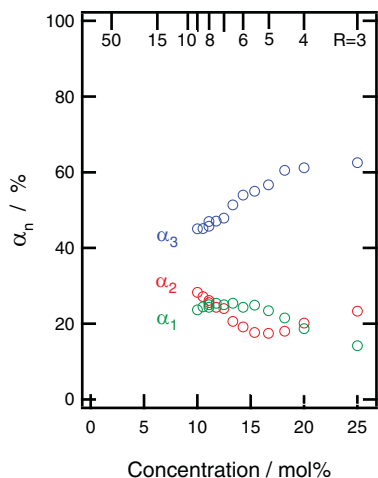


FIG. 5. Concentration dependences of a ratio of A_n ($\alpha_n = A_n/\Sigma A_n$) in $\chi''_{VV}(\nu)$. The α_1 , α_2 , and α_3 are presented by green opened circle, red opened circle, and blue opened circle, respectively. The concentration dependence of α_4 is not shown in this figure.

that the state of solvent water in the glassy LiClaq solution of 14.3 mol% ($R = 6$), which corresponds to the first hydration shell, may relate to the state of the HP-relaxed HDA and that the state of solvent water in the glassy LiClaq solution of 10.0 mol% ($R = 9$), which corresponds to excess water beyond the first hydration shell, may relate to the state of the 1 atm-relaxed HDA. This indicates that the molecular configuration of solvent water in glassy LiClaq solution might be HDA-like rather than LDA-like. The result of neutron diffraction study has suggested that the water structure in the glassy concentrated LiClaq solution ($R = 6$) and in relaxed HDA is almost the same.³³ Our conclusion sustains this result.

The concentration dependence of ν_1 for the glassy LiClaq solutions correlates to the concentration dependence of the specific volume for the glassy LiClaq solutions.²⁶ This indicates that the ν_1 increases as the specific volume of glassy LiClaq solution decreases. This volume dependence of ν_1 for glassy LiClaq solution is the same as the volume de-

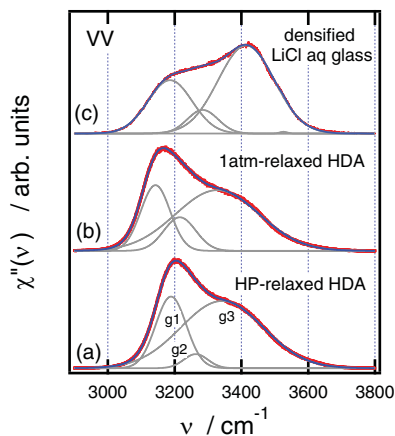


FIG. 6. Polarized (VV) reduced Raman spectra for (a) the HP-relaxed HDA, (b) the 1 atm-relaxed HDA, and (c) the densified glassy LiCl aqueous solution (11.1 mol%; $R = 8$) in the OH-stretching region. Red dots denote the measured Raman spectra. Blue line denotes results analyzed by a linear combination of some Gaussian functions (gray lines).

pendence of ν_1 for HDA and opposite to the volume dependence of ν_1 for crystalline ices. Generally, when crystalline ice is compressed isotropically the ν_1 decreases with the volume decreases.³⁰ The decrease of ν_1 for the crystalline ices is caused by the softening of OH-stretching vibration due to the shortening of the hydrogen bond distance between water molecules. However, when the crystal-to-crystal phase transition occurs by the further application of pressure, the volume decreases distinctly but the ν_1 increases.³⁰ The increase of ν_1 at the crystal-to-crystal phase transition is caused by the modification of topological molecular configuration. Therefore, we consider that the changes of ν_1 for the relaxed HDA and for the glassy LiClaq solutions relate to the change in the glassy state due to the modification of molecular configuration.

In Fig. 6(c), we show the $\chi''_{VV}(\nu)$ of the densified glassy LiClaq solution (11.1 mol%; $R = 8$) made by compression of the glassy LiClaq solution up to 1.5 GPa at 77 K at 0.15 GPa/min.²² The ν_1 of the densified glassy LiClaq solution are presented in Fig. 3 (solid square). The ν_1 of the densified glassy LiClaq solution is shifted to the higher frequency side by the densification as shown by the arrow in Fig. 3 and its value agrees with the value of ν_1 for the glassy LiClaq solution of 14.3 mol% ($R = 6$). Moreover, its Raman profile is similar to that of the glassy LiClaq solution of 14.3 mol% ($R = 6$). This indicates that the solvent state of the densified glassy LiClaq solution of 11.1 mol% ($R = 8$) is analogous to that of the glassy LiClaq solution of 14.3 mol% ($R = 6$) which we made by cooling at 1 atm. In other words, since the pressure-induced densification of glassy materials relates to the structural relaxation,²² the state of excess water beyond the first hydration shell may deform to a state that is similar to a state of the first hydration shell. This is reasonable because we know that the 1 atm-relaxed HDA (which corresponds to the water molecules beyond the first hydration shell) relaxes to the HP-relaxed HDA (which corresponds to the first hydration shell) by the pressure-induced densification.²²

IV. CONCLUSION

The glassy LiClaq solutions (10.0–25.0 mol%; $R = 9$ –3) are made by rapidly cooling at 1 atm and their solvent states are studied using the polarized Raman spectroscopy. The concentration dependence of the g_1 mode reveals the difference between the state of water that is adjacent to the salt (namely, first hydration shell) and the state of the excess water beyond the first hydration shell (namely, second or third hydration shell). From the comparison between the g_1 mode for the glassy LiClaq solutions and the g_1 mode for the relaxed HDAs, it is found that the ν_1 for the glassy LiClaq solution of 14.3 mol% ($R = 6$) agrees approximately with the ν_1 for the HP-relaxed HDA and that the ν_1 for the glassy LiClaq solution of 10.0 mol% ($R = 9$) is similar to the ν_1 for the 1 atm-relaxed HDA. These results suggest that the glassy state of water that is adjacent to the salt relates to the state of HDA under high pressure and the glassy state of excess water beyond the first hydration shell relates to the state of HDA under low pressure. In addition, the Raman profile of the densified glassy LiClaq solution of 11.1 mol% ($R = 8$) is similar to that of the glassy LiClaq solution of 14.3 mol%

($R = 6$) made by cooling under 1 atm. This indicates that the excess water beyond the first hydration shell is densified by compression and the densified solvent state is similar to the solvent state of the first hydration shell. This result is consistent with the pressure-induced relaxation of 1 atm-relaxed HDA to HP-relaxed HDA.²²

Previous studies relating to the hydration structure in electrolyte aqueous solutions show that the effect of salt on water in electrolyte aqueous solution at room temperature is equivalent to the effect of pressure on water.^{32–41} On the other hand, according to the water polyamorphism, water under high pressures is thought to relate thermodynamically to HDA.^{42–45} Therefore, we consider that the solvent state in glassy LiCl aq solution relates closely to the state of HDA. Moreover, the similarity between the state of excess water beyond the first hydration shell and the state of the 1-atm relaxed HDA suggests that the attenuation of the salt effect on water is equivalent to the attenuation of the pressure effect on water. This suggestion predicts a possibility that the nature of hydrophilic hydration may be HDL. In order to verify the validity of the speculation, it is necessary to understand the relation between hydrations and water polyamorphism further in the future.

ACKNOWLEDGMENTS

We are grateful to O. Mishima for many helpful discussions.

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