Gallium Trichloride Fluid: Dimer Dissociation Mechanism, Local Structure, and Atomic Dynamics

Maxim Khomenko [1,2], Anton Sokolov [3], Andrey Tverjanovich [4], Maria Bokova [3], Mohammad Kassem [3], Takeshi Usuki [5] and Eugene Bychkov [3,*]

[1] National Research Centre, Kurchatov Institute, Shatura, Moscow 140700, Russia; khomenkolaser@gmail.com
[2] Laboratory of Biophotonics, Tomsk State University, Tomsk 634050, Russia
[3] Laboratoire de Physico-Chimie de L'atmosphère, Université du Littoral Côte d'Opale, 59140 Dunkerque, France; anton.sokolov@univ-littoral.fr (A.S.); maria.bokova@univ-littoral.fr (M.B.); mohamad.kassem@univ-littoral.fr (M.K.)
[4] Institute of Chemistry, St. Petersburg State University, St. Petersburg 198504, Russia; andr.tver@yahoo.com
[5] Faculty of Science, Yamagata University, Yamagata 990-8560, Japan; usuki@kdw.kj.yamagata-u.ac.jp
* Correspondence: eugene.bychkov@univ-littoral.fr

SUPPORTING INFORMATION

Dissociation Reaction: Calculation Details

Figure S1. Mean-square displacements in normal liquid $GaCl_3$ at 400 K.

Figure S2. Experimental and FPMD-derived viscosity for molten $GaCl_3$.

Dissociation Reaction: Calculation Details

Let us consider the dissociation reaction:

$Ga_2Cl_6 \rightleftharpoons 2GaCl_3$. (S1)

The equilibrium constant, based on reported partial pressures[S1] (the insert in Figure 1a), can be written as

$$K_{\mathrm{p}} = \frac{P^2_{\mathrm{GaCl_3}}}{P_{\mathrm{Ga_2Cl_6}}} . \quad \text{(S2)}$$

The equilibrium constant, representing the molar fractions, is given by

$$K_{\mathrm{m}} = \frac{x^2_{\mathrm{GaCl_3}}}{x_{\mathrm{Ga_2Cl_6}}} = \frac{K_{\mathrm{p}}}{P_{\mathrm{total}}} . \quad \text{(S3)}$$

Solving the quadratic equation relating K_{m} and $x_{\mathrm{GaCl_3}}$ and taking into account that $x_{\mathrm{Ga_2Cl_6}}$ + $x_{\mathrm{GaCl_3}}$ = 1, one obtains the monomer molar fraction $x_{\mathrm{GaCl_3}}$ as a function of temperature for unsaturated vapor (Figure 1b).

The equilibrium constant depends on the total pressure in the system

$$\frac{d \ln K_{\mathrm{m}}}{dP} = -\frac{1}{P_{\mathrm{total}}} . \quad \text{(S4)}$$

By calculating $x_{\mathrm{GaCl_3}}$ at $P_{\mathrm{total}} = P_{\mathrm{c}}$ and $P_{\mathrm{total}} = 3P_{\mathrm{c}}$, one observes a decreasing monomer molar fraction (Figure 1b), consistent with the experimental and FPMD results.

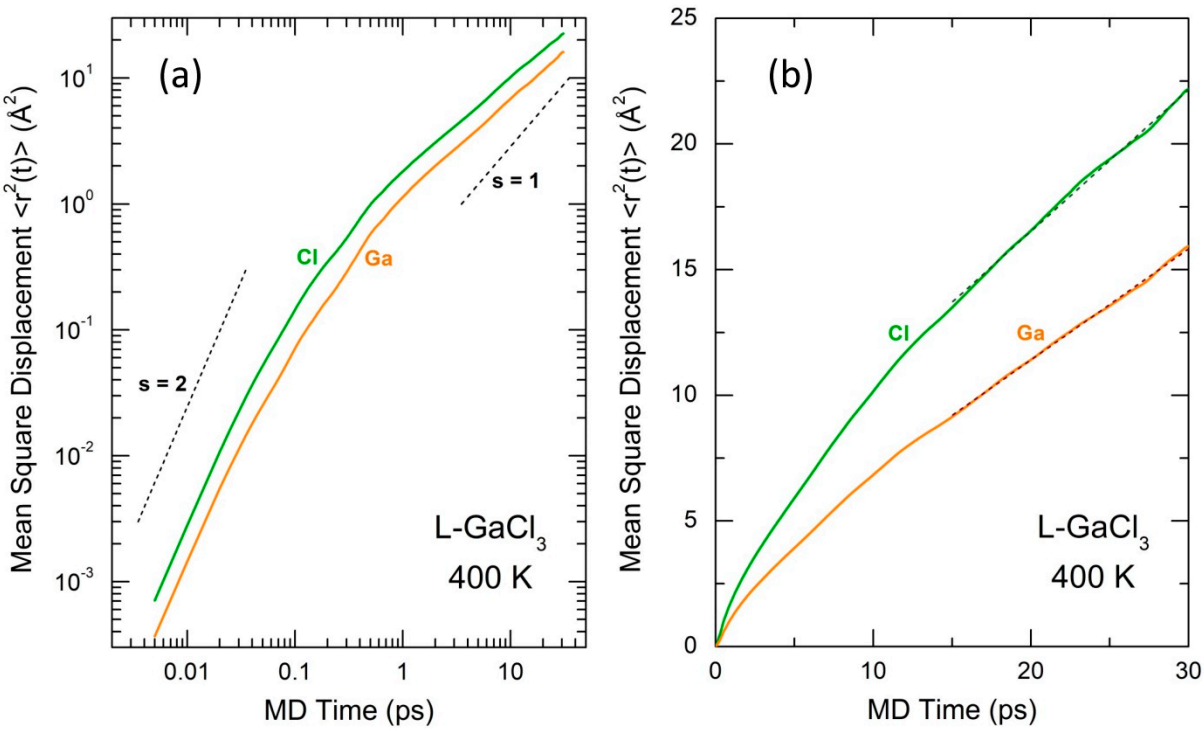

Figure S1. Mean-square displacements in normal liquid $GaCl_3$ at 400 K: (a) log-log scale, (b) linear scale. The slopes for ballistic regime (s = 2) and diffusion regime (s = 1) are shown in (a).

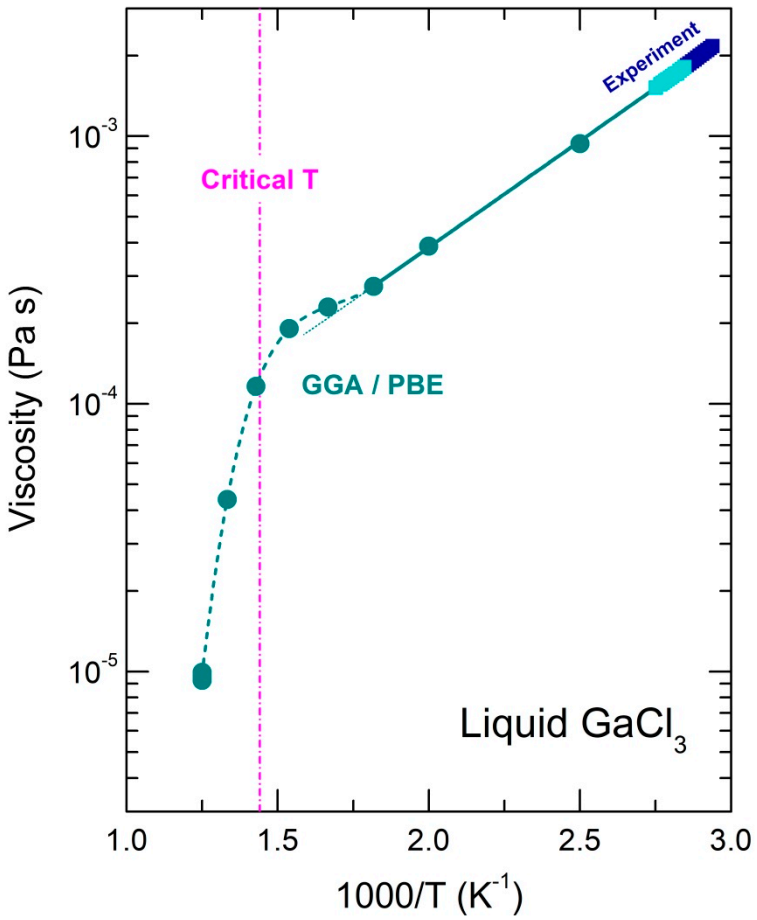

Figure S2. Experimental[S2] and FPMD-derived viscosity for molten $GaCl_3$.

Additional References

S1. Fischer, W.; Jübermann, O. Über thermische Eigenschaften von Halogeniden. 10. Dampfdrucke und Dampfdichten von Gallium III – Halogeniden. *Z. Anorg. Allg. Chem*. **1936**, *227*, 227–236.

S2. Greenwood, N. N.; Wade, K. Some Physical Properties of Molten and Supercooled Gallium Trichloride. *J. Inorg. Nucl. Chem*. **1957**, *3*, 349–356.