Supplementary Information: Nuclear Quantum Effects on the Liquid-Liquid Phase Transition of a Water-Like Monatomic Liquid

We include a complementary analysis of the structure of the studied FJ liquids based on the local orientational order parameter Q_6 , defined in Ref. [1], and the translational order parameter t_p , defined in Ref. [2]. In both cases, the parameters are defined in terms of the coordinates of the atoms centroids. We employ these parameters to discriminate efficiently the presence of crystallization.

Figs. 1(a) and 1(b) show, respectively, Q_6 and t_p averaged over all atoms in the system. To show the nuclear quantum effects on the liquids structure, we present results at $h = h_1$, h_2 , h_3 and at the corresponding $T = T_c(h)$ (see Figs. 5 and 6 in the main manuscript). Fig. 1(a) shows that Q_6 increases monotonically with increasing v. In the HDL state, the (centroids) orientational order does not change as the quantumness of the liquid (quantified by h) increases, while minor changes in Q_6 occur in LDL [for example, at v = 3.4 (LDL), Q_6 increases by $\approx 10\%$]. We note that the system crystallizes at v = 3.6, as indicated by the sudden increase in orientational order. Similar changes are found in translational order [Fig.1(b)]. Specifically, while t_p barely changes with h at low volumes (HDL), a small increase in translational order occurs at large volumes [for example, at v = 3.4 (LDL), t_p increases by $\approx 15\%$]. Interestingly, the translational order parameter is a non-monotonic function of v, and exhibits a minimum at $v \approx 2.6 - 2.7$, slightly below the LLCP volume ($v_c \approx 2.9$).

Crystallization can be easily detected by monitoring the probability distribution to find an atom with local orientational order parameter $Q_{6,i}$, $P(Q_{6,i})$ (see Ref. [3, 4]). Specifically, as indicated, in Fig. 2(a)-(c), crystallization is accompanied by a sharp peak in $P(Q_{6,i})$ at $Q_{6,i} \approx 0.5$.

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- [2] J. R. Errington and P. G. Debenedetti, *Nature*, 2001, 409, 318.
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FIG. 1: (a) Orientational and (b) translational order parameters averaged over all atoms in the system. Results are for three quantum FJ liquids (Planck's constant $h_1 = 0.2474$, $h_2 = 0.5150$, and $h_3 = 0.7948$) at the corresponding LLCP temperature $T_c(h)$. The sudden increase in both parameters at v = 3.6 is due to crystallization.



FIG. 2: Probability distribution to find an atom with orientational order parameter $Q_{6,i}$, $P(Q_{6,i})$. (a) $h_1 = 0.2474$, (b) $h_2 = 0.5150$, and (c) $h_3 = 0.7948$. Crystallization is accompanied by a sharp peak in $P(Q_{6,i})$ at $Q_{6,i} \approx 0.5$.