New Understanding of Liquid Thermodynamics and Supercritical State

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Existing textbook expressions for the energy and heat capacity of gases and solids are widely taught in physics courses. However, no such expression exists for a liquid. The reason for this was summarized by Landau as "liquids have no small parameter", and discussed in some detail in Landau & Lifshitz Statistical Physics textbook. Based on the old idea of J Frenkel, I formulate the problem in the language of phonons, and calculate liquid energy and heat capacity for both classical and quantum cases. The resulting equation relates liquid heat capacity to its relaxation time with no fitting parameters, and is consistent with the experimental data of metallic, noble, molecular and network liquids [1]. The data includes several supercritical fluids from the NIST database. I subsequently discuss how thermodynamic properties of the liquid change above the critical point using the recent idea that the mean-free path defines the minimal wavelength of longitudinal phonons in the system and our recent finding of the crossover of liquid specific heat in the supercritical state [2]. I finally discuss the new Frenkel line recently proposed to exist in the supercritical state of matter [3]. Contrary to the existing view, we have shown that the supercritical state is not physically homogeneous in terms of physical properties, but exists in two distinct states: “rigid” liquids and “non-rigid” gas-like fluids separated by a dynamic transition across the Frenkel line on the phase diagram. All major properties of the system, including diffusion, viscosity, thermal conductivity, speed of sound and heat capacity as well as structure all undergo qualitative changes at the Frenkel line, from the liquid-like to gas-like [3,4].

References:

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