Comment on "Long-Ranged Orientational Order in Dipolar Fluids"

Recently Groh and Dietrich [1] calculated orientational order transitions for dipolar fluids contained in spheroidal shapes of aspect ratio k. According to their study the thermodynamic state of a dipolar fluid depends on the shape of the fluid's container. For example, a homogeneous fluid in a short fat container would phase separate when transferred to a tall skinny container of identical volume and temperature. Their calculation thus lacks a thermodynamic limit.

Existence of a thermodynamic limit for dipolar fluids has not previously been proven. Indeed, the long-range anisotropic dipole interaction presents significant difficulties. These include mathematical difficulties such as the conditionally convergent, shape dependent integrals examined by Groh and Dietrich. Physically, the long interaction range causes domain or texture formation to avoid demagnetization fields. Still, Griffiths [2] has proven the existence of a shape independent thermodynamic limit for the free energy of dipoles on lattices. So we presume that dipolar fluids also possess a thermodynamic limit.

The shape dependence in Groh and Dietrich's calculation results from their assumption of spatially uniform magnetization. Real crystalline ferromagnets form domains to avoid stray "demagnetization" fields which arise when the magnetization is not parallel to the sample boundary. In a liquid ferromagnet, however, the domain wall thickness is limited only by sample size [3]. Thus the magnetization is expected to rotate across the sample in a manner as yet undetermined. There is one sample shape which avoids the demagnetization field—the limit $k \to \infty$ corresponding to an infinitely prolate spheroid. The bulk free energy calculated for a uniform magnetization in this needlelike shape will match the true free energy of any shape with appropriate spatially varying magnetization.

While the $k \to \infty$ limit is the uniquely appropriate value for calculating bulk free energy density assuming a spatially uniform magnetization, we do not expect a real ferromagnetic liquid drop to take this needlelike shape in the absence of external field. The actual shape and magnetization texture of a ferromagnetic liquid droplet remains an important unsolved problem.

Taking $k \to \infty$ is not practical for computer simulations. Recent computer simulations [4–7] solve the long-range interaction problem by combining the Ewald summation with a reaction field [8]. The limit of infinite surrounding dielectric constant $\epsilon \to \infty$ cancels the demagnetization field and yields the true thermodynamic limit with a uniform state, while being computationally more tractable than taking $k \to \infty$. In simulations with $\epsilon = 1$, Weis and Levesque [4] find domain formation consistent with our assertion that demagnetization fields create spatially nonuniform states.

Now consider Groh and Dietrich's density functional theory phase diagram in the $k \to \infty$ limit. This contains a continuous magnetic transition at high temperatures and a tricritical point below which phase separation occurs between dilute isotropic gas and dense magnetized liquid. Simulations of hard [4] and soft [5,6] dipolar spheres place the magnetized liquid state at higher densities and lower temperatures than suggested by the present calculation. A simulation of the Stockmayer fluid [7] reveals isotropic phase separation with a conventional critical point. We believe the density functional theory may be brought into closer agreement with computer simulation by incorporating the effects of random particle positions which shift the magnetic transition to larger densities [9], and particle chaining [10] which competes with ordinary phase separation at strong dipolar coupling. Both effects require three-body and higher terms in the density functional theory.

The phase diagrams found by Groh and Dietrich illustrate part of a generic sequence of phase diagrams for dipolar fluids [11]. Many parameters, including the strength of the $1/r^6$ attraction in the Stockmayer fluid, carry the phase diagrams through such a sequence. But sample shape is *not* among such parameters.

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