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1989 J. Phys.: Condens. Matter 1 993

(http://iopscience.iop.org/0953-8984/1/5/015)

J. Phys.: Condens. Matter **1** (1989) 993–997. Printed in the UK

On the properties of fluids with dispersed superconducting particles

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Received 4 May 1988, in final form 19 September 1988

Abstract. A theoretical estimation is made of properties of the superdiamagnetic fluid and composite suspensions (colloidal solutions of particles of superconducting material dispersed in liquid solvent at $T < T_c$) that were previously proposed by the authors. It is shown that the superdiamagnetic fluid has an anomalously high initial diamagnetic susceptibility. It is further shown that such a fluid can be regarded as a model system for the investigation of phase transitions. The magnetisation curve of a composite suspension (in which a magnetic fluid serves as solvent) is investigated; the behaviour of this curve can be either para- or diamagnetic, depending on the applied magnetic field.

The discovery of superconducting materials with the critical temperature T_c above the nitrogen temperature (Sun *et al* 1987, Wu *et al* 1987) has stimulated the development of new approaches in the physics of condensed media. The present authors have already discussed (Kalikmanov and Dyadkin 1987) the possibility of preparation and the properties of 'superdiamagnetic fluid' (SDF), representing a colloidal solution of superconducting particles dispersed in a solvent retaining the liquid state at $T < T_c$. The base can be, say, Y–Ba–Cu–O ceramic ($T_c = 90$ K (Sun *et al* 1987)) and the solvent, liquid nitrogen (BP 77.4 K at normal pressure).

As regards its structure, SDF is analogous with a magnetic fluid (MF) (cf Berkovsky *et al* 1985, 1987), consisting of a colloidal suspension of ferromagnetic particles (Fe, Co, Ni, Fe_3O_4) dispersed in a solvent fluid (water, kerosene, hydrocarbons); each particle is coated with a surfactant to avoid coagulation.

As in the case of a magnetic fluid, the maximum particle size d in SDF is restricted by the condition of colloid stability: the particles suspended in the solvent must not settle in the gravitational field for a characteristic time, t, for the problem. As is known, in the state of thermodynamic equilibrium, the particle height distribution is subject to the Boltzmann barometric law:

$$n(z) \sim \exp(-\Delta\rho g V_0 z/kT) \tag{1}$$

where $\Delta\rho = \rho_s - \rho_l$ is the difference between the solid and liquid phase densities, V_0 is the particle volume, and k is the Boltzmann constant. The time t' for setting the equilibrium distribution for colloidal particles can be estimated as $t' \simeq h^2/D$, where h is the height of the container, $D \simeq kT/\eta d$ is the diffusion coefficient of suspended particles,

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and η is the solvent viscosity. Therefore

$$t' \simeq h^2 \eta d/kT. \tag{2}$$

For $d = d_{max} \simeq 10^{-4}$ cm (the maximum particle size for known stable colloids), $h \simeq 1$ cm, $T = 70$ K, and $\eta = 2 \times 10^{-3}$ g cm^{-1} s^{-1}, we obtain from (2) $t' \simeq 10^8$ s (one day $\sim 10^5$ s). So, the initially homogeneous system (SDF) remains homogeneous over a long period of time $t < t'$.

From below, d is restricted by the London penetration depth λ_L ($\lambda_L \sim 10^2$–10^3 Å). The mean particle size is determined from the condition $\lambda_L \ll d < d_{max}$. The solid phase concentration c is of the order of 10^{12}–10^{14} cm^{-3}.

Consider now the magnetostatic properties of SDF placed in an external magnetic field with an intensity $\boldsymbol{H}_e$. Due to the Meissner effect, every particle develops a magnetic moment $\boldsymbol{m} = \boldsymbol{M}_0(\boldsymbol{H}_e, T)V_0$, where $\boldsymbol{M}_0$ is the particle magnetisation. For particles with type-I superconductivity

$$\boldsymbol{m}(\boldsymbol{H}_e, T) = -[V_0/4\pi(1-D)]\,\boldsymbol{H}_e\theta(T_c - T)\theta[H_c(T) - H_e/(1-D)] \tag{3}$$

where D is the demagnetisation factor, $\theta(x) = 1$ at $x > 0$ and $\theta(x) = 0$ at $x \leqslant 0$, $H_c(T)$ is the critical field whose temperature dependence is given by the Gorter–Casimir formula (Lynton 1969): $H_c(T) = H_c(0)[1 - (T/T_c)^2]$. For particles with type-II superconductivity

$$\begin{aligned}\boldsymbol{m}(\boldsymbol{H}_e, T) = -[V_0/4\pi(1-D)](\boldsymbol{H}_e/H_e)\theta(T_c - T)\{&H_e\theta[H_{c1}(T) - H_e/(1-D)] \\ &+ f_m(H_e)\theta[H_e/(1-D) - H_{c1}(T)]\theta[H_{c2}(T) - H_e/(1-D)]\}\end{aligned} \tag{4}$$

where H_{c1} and H_{c2} denote the first and second critical fields, respectively, and $f_m(H_e)$ is the mixed-state curve (Saint-James *et al* 1969).

As distinct from MF in which the value of the magnetic moment of the ferroparticles is independent of the applied field, in SDF $\boldsymbol{m}$ depends fully on the field. Another distinction is that in MF the Brownian motion (kT) has a disordering effect on magnetic moments while in SDF, at any temperature $T < T_c$, $\boldsymbol{m}$ is antiparallel with $\boldsymbol{H}_e$ because the time for Meissner relaxation (about 10^{-10} s) is several orders of magnitude less than the time for Brownian diffusion $\tau_B = 3V_0\eta/kT$ (about 10^{-4}–10^{-2} s). The magnetisation of MF is of Langevin type with a saturation M_s of the order of 20–50 G in fields of 0.05–0.1 T (Berkovsky *et al* 1987). It follows from equations (3) and (4) and the preceding remark that, up to H_c (up to H_{c1}, in the case of type-II superconductors), the magnetisation of SDF is linear over the field:

$$\boldsymbol{M} = -[1/4\pi(1-D)]\varphi\boldsymbol{H}_e\theta(T_c - T) \tag{5}$$

($\varphi = cV_0$ is the volume concentration of the solid phase), and then drops (logarithmically, in the case of type-II superconductors); at the point $H_e/(1-D) = H_c(H_e/(1-D) = H_{c1}$ for type-II superconductors) the function $M(H_e)$ is non-analytic. It is to be noted that (5) is valid for small values of φ when the particle interaction can be ignored.

The initial susceptibility of SDF $\chi = -[1/4\pi(1-D)]\varphi\theta(T_c - T)$ does not depend on T (at $T < T_c$) and is governed only by the volume particle concentration φ. The likely values of χ of the order of 10^{-2}–10^{-3} for SDF, are three to four orders of magnitude greater than in the case of natural diamagnetics, which justifies the introduction of the term 'superdiamagnetic fluid'.

The Brownian rate of particle motion for SDF, v_B, is of the order of 0.1–0.3 cm s^{-1}. Following binary collision, the particles travel a distance b of the order of 10 Å over a

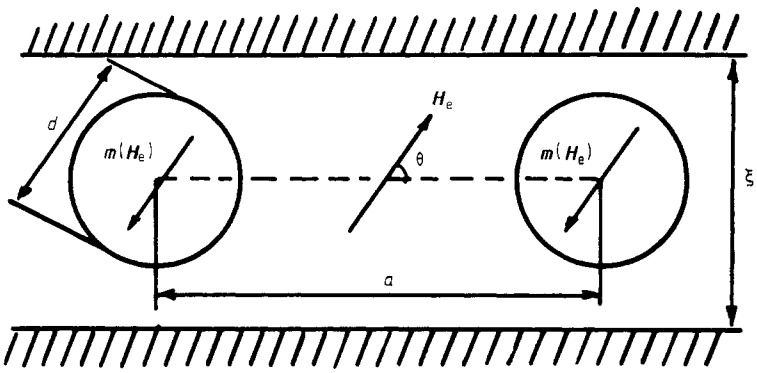

Figure 1. The plane layer of SDF in magnetic field.

period of time $\tau = b/v_B \sim 10^{-6}$–$10^{-7}$ s, which is much longer than the time of electron tunnelling across a thin layer of solvent with a width b. Consequently, a tunnel superconductivity current may flow between the particles (the Josephson effect) during the time τ after collision. Therefore, from the standpoint of superconductivity, SDF is a system of disordered dynamic Josephson contacts. The possibility of realising slight superconductivity in such a medium appears rather intriguing and calls for separate study.

One further range of problems is associated with the fact that SDF can be regarded as a model system for studying many-particle phenomena in condensed state physics; monodisperse particles of SDF present a macroscopic analogue of atomic systems. In so doing, fairly large particle sizes (of the order of 0.1–1 μm) permit the observation of processes occurring in SDF with the aid of optical or electron microscopy (a model system of this kind representing a suspension of polystyrene spheres in magnetic fluid was considered by Skjeltorp (1983)). Such processes include melting, crystallisation, aggregation and so on.

Let us now consider a thin layer of SDF with a thickness $\xi \geqslant d$ placed in a field $\boldsymbol{H}_e$ (figure 1). The (spherical) particle interaction in such a two-dimensional (2D) system is a dipole–dipole one with the energy

$$U^{dd}(H_e, \theta) = [m^2(H_e)/a^3](1 - 3\cos^2\theta) \tag{6}$$

where θ is the angle between $\boldsymbol{H}_e$ and the layer plane, and a the distance between the centres of particles. As seen from (6), this interaction can be both attractive and repulsive, depending on the field direction (i.e., on the angle θ). If $\boldsymbol{H}_e$ is perpendicular to the layer ($\boldsymbol{H}_e = \boldsymbol{H}_{e\perp}$), there is mutual repulsion between the particles leading to the formation of an ordered 2D structure. Its stability depends on the ratio between U^{dd} and the energy of heat motion (kT). For the fields $H_{e\perp}$ that are less than H_{c1} ($H_{c1} \simeq 500$–1000 Oe), this ratio can be written as (using equation (4))

$$\gamma \equiv U^{dd}/kT = [V_0/4\pi(1 - D)]^2 (H_{e\perp}^2/a^3 kT).$$

The condition $\gamma \gg 1$ corresponds to the 'solid state phase', and the condition $\gamma \leqslant 1$ to the 'liquid phase'. For $d = 1$ μm, $H_{e\perp} = 100$ Oe, $a = 2$ μm and $T = 70$ K, we obtain $\gamma \simeq 700$. This value is much higher than the critical value $\gamma_c \simeq 62$ obtained using the method of molecular dynamics (Bedanov *et al* 1982). Consequently, by reducing $H_{e\perp}$ (and leaving the temperature unchanged), one can study 2D melting.

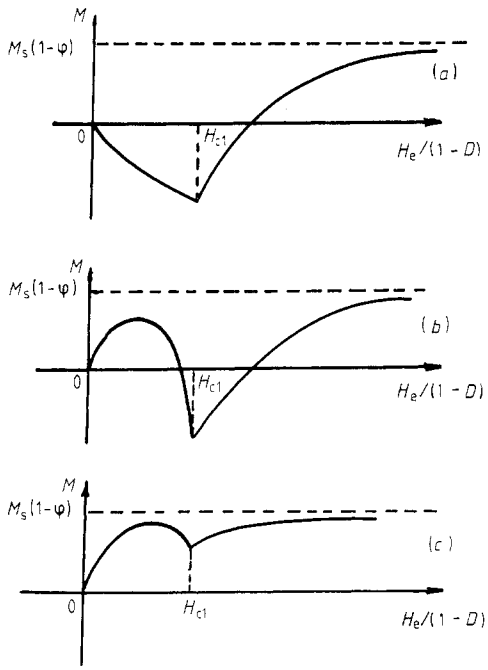

Figure 2. Magnetisation curves for composite suspensions.

A suspension of superconducting particles (of the same size $d \sim 10^3$–10^4 Å) in *magnetic fluid* for $T < T_c$ could possess very unusual properties. Consider now the magnetisation curve of such a 'composite suspension'. Since the size of the superconducting particles is one to two orders of magnitude greater than the size of MF ferroparticles, the superconducting particles will move against a homogeneous magnetic fluid background. Ignoring (for qualitative assessment) the inter-particle interactions, the magnetisation of composite suspension can be expressed as

$$\boldsymbol{M} = \boldsymbol{M}^{\mathrm{MF}}(1 - \varphi) + \boldsymbol{M}^{\mathrm{SDF}}$$

where $\boldsymbol{M}^{\mathrm{MF}} = \boldsymbol{M}_s L(sH_e/kT)$ is the magnetisation of MF in the absence of superconducting particles, s the magnetic moment of ferroparticles, M_s the saturation magnetisation of MF, $L(x)$ Langevin's function, and $\boldsymbol{M}^{\mathrm{SDF}}$ the magnetisation of SDF in the absence of MF; the factor $(1 - \varphi)$ allows for the excluded-volume effect. Let the inequality

$$|\chi^{\mathrm{SDF}}| = \varphi/4\pi(1 - D) > \chi^{\mathrm{MF}}$$

be satisfied for the initial susceptibility χ^i (i = SDF, MF). Then, the magnetisation curve of the composite suspension will be as shown in figure 2(a).

Figure 2(b) corresponds to the case $\varphi/4\pi(1 - D) < \chi^{\mathrm{MF}}$ and to

$$\varphi H_{c1}/4\pi(1 - D) > M_s L(sH_{c1}/kT)(1 - \varphi). \tag{7}$$

Finally, if the inequality (7) is not satisfied, we will obtain the curve shown in figure 2(c). Note that in cases (a) and (b) the behaviour of the composite suspension may be either para- or diamagnetic, depending on the magnitude of the applied field.

Therefore, the proposed colloidal systems based on superconducting materials may

possess a number of unusual properties. These include an anomalously high initial diamagnetic susceptibility, a non-analytic magnetisation curve that is capable (in the case of composite suspension) of changing the sign, and dynamic Josephson contacts. Such systems may also serve for modelling phase transitions in condensed state physics.

Acknowledgments

We are grateful to Professor V M Lazebnik, Dr B P Prokofiev and Dr V S Filinov for helpful discussions.

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