RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 35, NUMBER 2 JANUARY 15, 1987

Computer simulation of a classical fluid with internal quantum states

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(Received 22 October 1986)

We present simulation results on phase transitions in a fluid system whose interactions depend on internal quantum states: They are "turned on" when the molecules are in the hybrid state. Surprisingly, a simple effective temperature-dependent classical potential describes well many features of the transition.

The relationship between the cooperative behavior of macroscopic systems and the internal states of the component molecules is a subject of considerable theoretical and practical importance.[1-4] While the former can in many cases be treated classically, the latter are inherently quantum mechanical. This makes the study of such systems, particularly by computer simulation, much more difficult. As a result little is yet known about their properties.

However, with the advent of more powerful computers, there is now promise of real progress, Ref. 1. To date the investigations have been restricted mainly to lattice models. In particular, there have been no systematic computer-simulation studies of the effects of the internal quantum states on phase transitions in continuum systems. To our knowledge the only exception is the study by Hall and Wolynes of a model of supercritical mercury[2] (an explanation for the behavior of this element had already been proposed[3]). They make the important simplifying assumption that the mass M of the particles is so large that the translational degrees of freedom can be treated classically. However, the long-range interaction employed in this model limits the computation to very small systems and to a few thermodynamic state points.

In this paper, we present for the first time simulation results on phase transitions in a system of molecules with two internal quantum states which influence the interparticle interaction. In restricting ourselves to a simpler model than that studied by Hall and Wolynes we are able to perform a systematic quantitative study of phase transitions in fluid systems with intrinsic (annealed) disorder and quantum behavior.

The results of our simulations are compared with those obtained in the quantum mean-field approximation of Stratt[4] and show qualitative agreement. We then introduce effective one- and two-body classical potentials which reproduce to a great extent the important quantum effects, at least up to moderate values of the inverse temperature. We also compare our simulation results on the classical system to predictions obtained from the hypernetted-chain (HNC) approximation and find excellent agreement.

Description of the model. We consider a system of N particles in a d-dimensional periodic box with the following Hamiltonian:

$$H=\sum_{i=1}^{N}\frac{p_i^2}{2M}-\frac{\omega_0}{2}\sum_{i=1}^{N}\sigma_i^x+\sum_{\substack{i,j\\(i<j)}}U(\mathbf{r}_i-\mathbf{r}_j)-\sum_{\substack{i,j\\(i<j)}}J(\mathbf{r}_i-\mathbf{r}_j)\sigma_i^z\sigma_j^z\ ,$$

where p_i is the momentum and M the mass of the particles. $U(r)$ and $J(r)$ are short-range functions; σ^x and σ^z are the usual Pauli spin-$\frac{1}{2}$ matrices. We think of the particles as two-state molecules with an internal Hamiltonian $-\omega_0\sigma^x/2$, interacting via a pair potential, depending on their internal state. The interaction term will tend to lift particles out of their internal ground state corresponding to $\sigma^x=1$ into a hybrid state, i.e., the eigenstates of σ^z. Fixing the positions of the particles on a one-dimensional lattice makes this a well-known, exactly solvable model much studied in the literature.[5-7] However, little is known about the fluid systems considered here.

The classical-quantum partition function of the system has the following form (we set $h=1$):

$$Z=\frac{1}{N!}\int d\mathbf{r}_1\ldots d\mathbf{r}_N d\mathbf{p}_1\ldots d\mathbf{p}_N\,\mathrm{Tr}_{\mathrm{spins}}\exp(-\beta H)\ .$$

Following Suzuki,[6] we use the Trotter formula to write Z as

$$Z=\lim_{P\to\infty}\frac{A_P^{NP}}{\lambda^{Nd}N!}\int d\mathbf{r}_1\ldots d\mathbf{r}_N\exp\left[-\beta\sum_{\substack{i,j\\(i<j)}}U(\mathbf{r}_i-\mathbf{r}_j)\right]\times\sum_{\{s\}}\exp[-\beta V_P(\{s\})]\ ,$$

where

$$-V_P(\{s\})=\sum_{i=1}^{N}\sum_{j=1}^{P}\left[K_P s_{i,j}s_{i,j+1}+\frac{1}{P}\sum_{k=i+1}^{N}J(\mathbf{r}_i-\mathbf{r}_k)s_{i,j}s_{k,j}\right]\ .$$

A_P and K_P are defined as

$$A_P = [\tfrac{1}{2}\sinh(\beta\omega_0/P)]^{1/2} ,$$

$$K_P = \frac{1}{2\beta}\ln[\coth(\beta\omega_0/2P)] ,$$

and λ is the thermal wavelength. V_P is the Hamiltonian of an Ising-like classical system of P layers.

The properties of the system can now be obtained as thermal averages over the distribution

$$\exp\left[-\beta\sum U(r_i - r_j) - \beta V_P(\{s\})\right] .$$

The possibility of using computers to evaluate these averages relies on the demonstration by Suzuki and coworkers[7] that a reasonably small value of P can be enough to approximate the $P \to \infty$ limit.

Results. We have performed simulations of a three-dimensional system of hard spheres with diameter R and with a spin-dependent interaction $J(r)$ of the square-well form, extending to a distance $R+\Delta$: $J(r) = J_0\theta(R+\Delta-r)$ [$\theta(x)$ is the Heaviside function]. The interesting feature of the model is the dramatic increase of the cooperative behavior of the system with increasing density, coupled to the increasing occupation of the σ^z-dominated hybrid levels. At moderate values of β this leads to a second-order phase transition, while at higher values of β the transition becomes first order (compare, for instance, Ref. 8 for a discussion). We will report details of the phase diagram in a subsequent paper; here we discuss some of the interesting quantum features of the system near the second-order transition. The cooperative quantum effects are clearly seen in Fig. 1, which shows the sharp increase of the energy associated with the one-body Hamiltonian and the similar decrease of the spin-spin energy with increasing density. The second-order nature of the magnetic transition is illustrated by the plot of the susceptibility $\chi(\rho)$. The position of the peak of $\chi(\rho)$ can be used as a reasonable estimate of the location of the transition.[9] Anomalies, similar to those shown by $\chi(\rho)$, occur for the specific heat and the compressibility of the system. We are planning a more systematic investigation of the properties of the system near the transition using finite-size scaling techniques. Preliminary investigation of larger systems confirms the accuracy of our rough estimates on ρ_c.

Figure 2 shows the transition densities ρ_c as a function of βJ_0 for different values of $\beta\omega_0/2$. The interval of βJ_0 displayed has been restricted to the region of the phase diagram in which we have only a second-order transition. The dashed lines show the predictions of the mean-field theory as discussed by Stratt.[4] This simple scheme seems to reproduce quite well the qualitative features of the transition line, if not the quantitative ones. We expect the

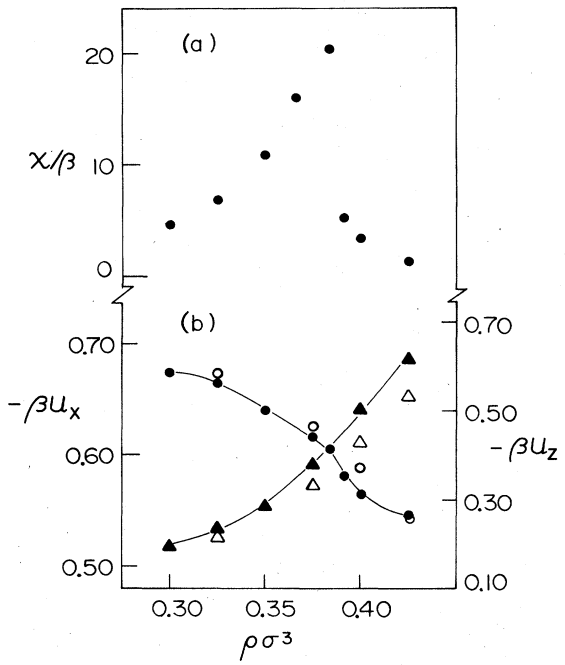

FIG. 1. (a) Susceptibility χ as a function of density ρ for the system with $\beta\omega_0/2 = 1$ and $\beta J_0 = 0.35$. The values of the other parameters described in the text are $\Delta = 0.5R$, $N = 250$, and $P = 16$. The position of the peak of $\chi(\rho)$ provides an estimate of the density of the "paramagnetic-ferromagnetic" transition. (b) For the same system as in (a) the circles represent the energy u_x due to the one particle operator $-\frac{1}{2}\omega_0\sum\sigma_i^x$ and the triangles the energy u_z due to the spin-spin interaction. The filled and empty symbols refer to the quantum Monte Carlo simulations and the equivalent classical system, respectively. The lines have been added only as a guide.

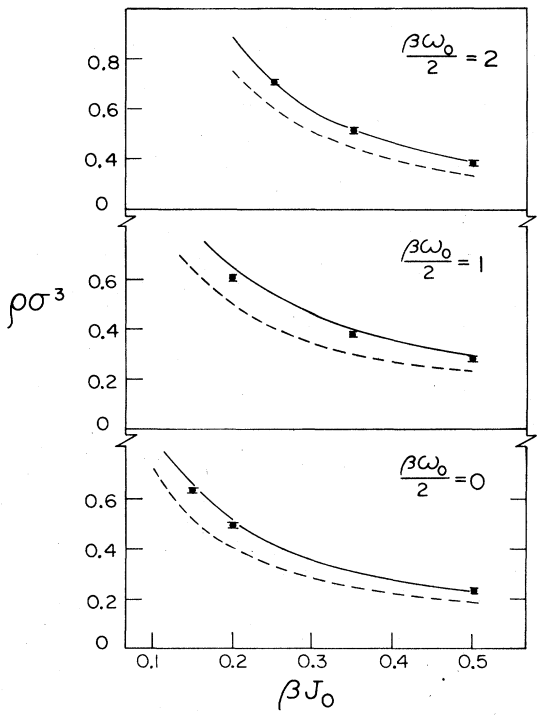

FIG. 2. Density of the "paramagnetic-ferromagnetic" transition as a function of $\beta J_0(\Delta = 0.5R)$ for three different values of $\beta\omega_0/2$. The filled circles are the results of the simulation; the full lines give the predictions of the HNC approximation and the dashed curve lines that of mean field (Ref. 4).

agreement to improve with increasing Δ as this permits the simultaneous interaction of a larger number of molecules. It should correspondingly become poorer as Δ is decreased.

Effective potentials. While the Trotter formula gives a possibility of simulating a quantum-mechanical system it would be useful to be able to describe our system by one with a simple classical effective interaction. This idea, which goes back to at least Feynman,[10] would allow the application of well-known approximation techniques. We note that the effect of the term $\frac{1}{2}\omega_0\sum\sigma_i^x$ in the Hamiltonian is to provide a one-body contribution to the internal energy and to reduce the effective "dipole" of the particles. Therefore we model the quantum system with the following classical Hamiltonian:

$$\bar{V}=N\psi-\sum_{\substack{i,j\\(i<j)}} J(\mathbf{r}_i-\mathbf{r}_j)\bar{s}_i\bar{s}_j,\ \bar{s}_i=\pm s_{\text{eff}}\ ,$$

where ψ is a one-body potential which reproduces the free energy of the independent particles and s_{eff} is chosen in such a way to reproduce the free energy of two interacting particles:

$$\psi=-\frac{1}{\beta}\ln\cosh(\beta\omega_0/2)\ ,$$

$$\cosh(\beta J_0 s_{\text{eff}}^2)=\tfrac{1}{2}\{\cosh(\beta J_0)+\cosh[\beta(J_0^2+\omega_0^2)^{1/2}]\}\operatorname{sech}^2(\beta\omega_0/2)\ .$$

This simple prescription is able to fit reasonably well the properties of the quantum systems described above (at least for moderate values of β). This is apparent from Fig. 2 where the full line shows the transition density for the equivalent classical model computed in the HNC approximation. Simulations for the equivalent classical model confirm the HNC results.

The inclusion of many-body contributions should offer a systematic way of improving the quantum-classical correspondence. However, we believe the advantages of the present scheme are its simplicity and the possibility that it offers for obtaining quick estimates of the properties of the quantum system by exploiting the methods of classical statistical mechanics.

In conclusion, we have demonstrated (a) the feasibility of studying phase transitions of fluids with quantum internal degrees of freedom, (b) the possibility of approximating quantum effects by a classical Hamiltonian (at least in our system), (c) the semiquantitative agreement of the effective classical simulation results with those given by the HNC approximation, and (d) the qualitative validity of the quantum mean-field approximation.

We thank the Center for Materials Science at Los Alamos where some of the simulations were performed. We are also grateful to Jim Gubernatis for useful discussions. This work was supported by the Air Force Office of Scientific Research (AFOSR) Grant No. 82-0016C. The work of one of us (E.W.) was supported by AFOSR Contract No. S-49620-85-C-0019, and another (Ph.S.) received support from the Belgian Nationaal Fonds Voor Wetenshcappelÿk Onderzoek.

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