Structure and Dynamics of Bipolarons in Liquid Ammonia

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The behavior of singlet- and triplet-state bipolarons in liquid ammonia has been studied by quantum simulation. The singlet-state electron density is a peanut-shaped cavity structure with peaks in the distribution about 7 Å apart, whereas the triplet-state electron density consists of two distinct cavities. These findings are consistent with a large number of experimental observations and with a model proposed by Mott. In the singlet state, the dynamics of the electrons is characterized by novel hopping events.

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Metal-ammonia solutions have been studied extensively by scientists since their discovery in the nineteenth century [1,2]. In broad terms, the behavior of such solutions can be divided into four distinct regimes: A very-low-density region characterized by isolated excess electrons $\rho < 0.1$ mole percent metal (MPM), a slightly higher-density region $\rho < 2$ MPM dominated by spin-paired species (bipolarons), a liquid metal $\rho > 4$ MPM, and a high-density form characterized by metallic solid compounds with units of the form $M(NH_3)_n$ [1,2].

While considerable progress has been made in the study of solvated electrons and the low concentration regime [3,4], very little is known about the microscopic structure and dynamics of metal-ammonia solution in the 1-MPM concentration range. That spin-paired species are present can be inferred from the susceptibility which has its minimum at this density [1,2]. Moreover, the pairing must be rather weak as the absorption spectrum is relatively unchanged from the low-density regime and at very low concentration the bipolarons dissociate [1,2]. To explain these results, Mott has postulated an electron distribution resembling a hydrogen molecule but with a binding energy of a few tenths of an eV [5]. The dynamical behavior of this state was not discussed.

In order to more fully understand this part of the metal-ammonia phase diagram, we have performed Car-Parrinello calculations [6] based on local-spin-density-functional theory [7] for both singlet- and triplet-state bipolarons at a density of ~ 1 mole percent electrons (MPE). Such calculations allow the determination of both the structure and dynamics of the solvated electrons on the ground-state surface [6,8,9]. In our calculations, the ideas of Mott concerning the peanut-shaped cavity and the binding energy are quantified. In addition, we have identified a novel diffusion mechanism for the bipolaron.

It is now known that ammonia retains its gas-phase geometry throughout the metal-ammonia phase diagram [10]. The ammonia molecules were therefore represented by a rigid point-charge model [11]. The potential parameters were fitted to the properties of liquid ammonia. A simple pseudopotential which includes the polarizability of nitrogen atoms, Pauli repulsion, and the Coulomb interaction with the fixed charges of the solvent molecules was used to approximate the electron-ammonia interactions. This pseudopotential, which was fitted to the binding energy of an electron to small metal-ammonia clusters [12], was also found to reproduce the behavior of a single excess electron quite well [13]. With these potentials, a system containing 256 ammonia molecules and two electrons was studied at the state point $\rho_{NH_3} = 0.023$ Å^{-3}, $T = 260$ K in both the singlet and triplet electronic states.

The energy of the electronic states of the system was determined using local-spin-density-functional theory [7,14]. In this theory, the energy of an N-electron system is

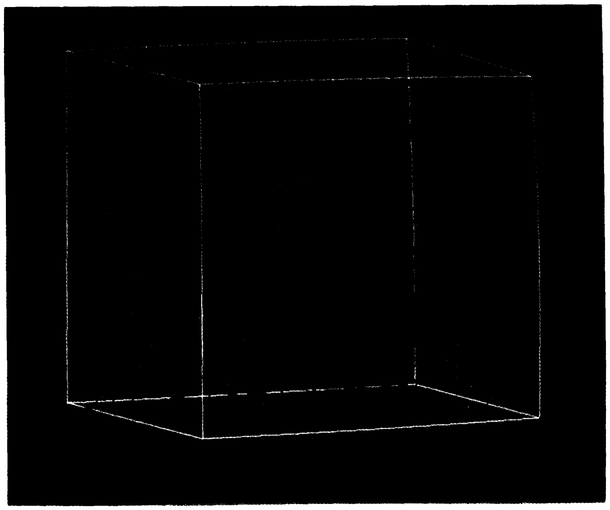
$$E[n(\mathbf{r})] = -\frac{\hbar^2}{2m}\int d\mathbf{r}\sum_{i,\sigma}\psi_{i\sigma}(\mathbf{r})\nabla^2\psi_{i\sigma}(\mathbf{r}) + \int d\mathbf{r}\, v(\mathbf{r})n(\mathbf{r}) + \frac{1}{2}\int\int d\mathbf{r}\, d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n_1(\mathbf{r}), n_{-1}(\mathbf{r})]\,, \quad (1)$$

where $n(\mathbf{r}) = n_1(\mathbf{r}) + n_{-1}(\mathbf{r})$, $n_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma}|\psi_{i\sigma}(\mathbf{r})|^2$, and $N_1 + N_{-1} = N$. The self-consistent equations for the orbitals are then

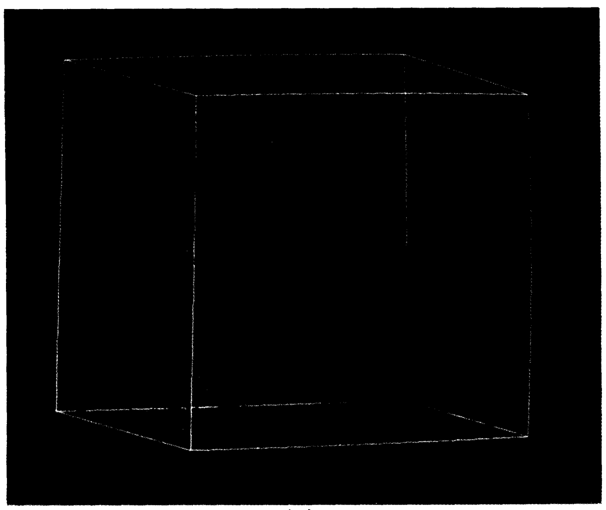
$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v(\mathbf{r}) + \int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}(\mathbf{r})}{\delta n_\sigma(\mathbf{r})}\right]\psi_{i\sigma}(\mathbf{r}) = \epsilon_i\psi_{i\sigma}(\mathbf{r})\,, \quad (2)$$

where the exchange-correlation energy is defined as $E_{xc}(\mathbf{r}) = \int d\mathbf{r}\, n(\mathbf{r})[\epsilon_x(\mathbf{r}) + \epsilon_c(\mathbf{r})]$. The form of the spin-polarized $\epsilon_x(\mathbf{r})$ and $\epsilon_c(\mathbf{r})$ are taken from Perdew and Zunger [7]. The singlet electronic state is determined by solving this set of equations for the ground-state spin-up and spin-down orbitals. The triplet state is determined by constraining the ground-state spin-up orbital and the ground-state spin-down orbital to be orthogonal. A plane-wave basis set was used to expand the orbitals with a cutoff of $k_{max} = 14\pi/L$, where L is the size of the simulation cell.

The structure and dynamics of the system were determined using the Car-Parrinello method [6,15]. The



(a)



(b)

FIG. 1. The electron density of representative configurations of (a) singlet and (b) triplet bipolarons taken from the present calculations which consist of 256 ammonia molecules and two electrons in a periodically replicated cell of edge 22 Å. The outermost contour contains 95% of the electron density.

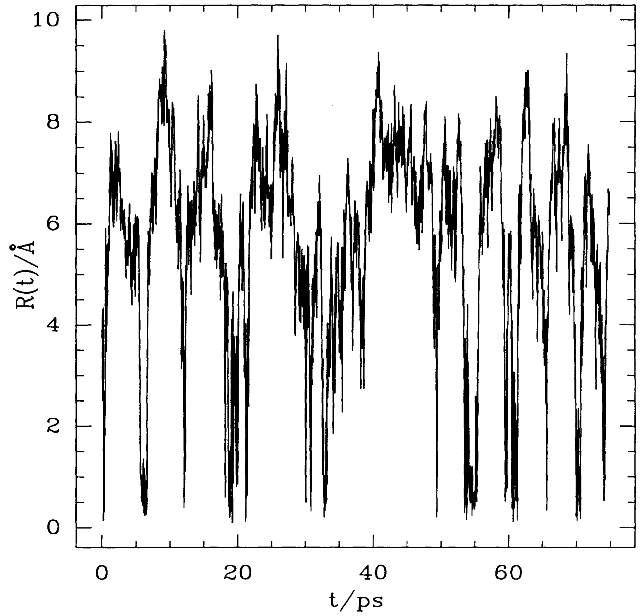


FIG. 2. The distance between the average position of the spin-up density and the average position of the spin-down density, as a function of time for the singlet-state bipolaron in liquid ammonia (see text).

coefficients of the plane-wave basis set are given a fictitious momentum and the system propagated according to a Lagrangian consisting of the electronic energy, the solvent potential energy, the solvent kinetic energy, and the fictitious momentum. In addition, independent Nosé thermostats were placed on the solvent atoms to keep them at a temperature of 260 K and on the basis-set coefficients to keep them at a temperature of 0.02 K [16]. The mass of the basis-set coefficients was then adjusted until an adiabatic separation between the electronic and the solvent degrees of freedom was attained, $m_{\mathrm{basis}}=256$ a.u. This separation ensures evolution on the ground-state electronic surface. Independent thermostats were placed on the solvent translational and rotational degrees of freedom with masses $30000(N_{\mathrm{mol}})$ a.u. and $2000(N_{\mathrm{mol}})$ a.u., respectively. The thermostats for the spin-up and spin-down orbitals were also assumed to be independent, each with mass 32 a.u. Simulations were run for 50 ps using the Verlet integration algorithm and a time step of 16 a.u. The Shake algorithm was used to apply the orthogonality constraints [6]. Further details will be presented in another publication [17]. The results of the present Car-Parrinello calculation for the singlet state have been confirmed by path-integral Monte Carlo studies, which gives us confidence in the method outlined above [17].

The equilibrium structure of the singlet- and triplet-state bipolarons in liquid ammonia at ~1 MPE are very different. Figure 1 compares two representative configurations taken from the present simulations. In the singlet state, on average the electrons assume a peanut-shaped distribution with the peaks in density about 7 Å apart [Fig. 1(a)]. However, in the triplet state, the electrons form two distinct spherical cavities [Fig. 1(b)]. The energy of the singlet state is lower than that of the triplet state at this density by ~0.6 eV and lower than that of two excess electrons at infinite dilution by ~0.3 eV (energies not free energies). Given these rather small stabilization energy differences, triplet-state calculations were also initialized in representative singlet-state cavities, and singlet-state calculations were started in representative triplet-state cavities to verify the above results. Indeed, after a suitable period of equilibration, the previous distributions reappeared. Thus, our results confirm the postulates of Mott concerning the electron distribution in this region of the phase diagram and even the order of magnitude of the bipolaron binding energies [5].

In addition to confirming Mott's largely intuitive deductions, the present results give some information on the dynamical evolution of the system which has been the source of considerable speculation [18]. The results proved to be quite surprising. First, the dynamics of the singlet and triplet states are quite distinct. In the triplet state, the distance between the average spin positions oscillates quite benignly about its equilibrium value. In the singlet state, however, the behavior is characterized by quiescent periods of oscillation about the average separation followed by jumps to small bond length (see Fig. 2). Typically, the jumps occur at intervals of about 5 ps. Such jumps can occur because of a near cancellation between the electronic kinetic energy and the Coulomb repulsion. That is, as the electron distribution approaches zero bond length, rather than having electron density localized in the lobes of the peanut-shaped equilibrium cavity, the electrons can spread out and occupy a larger spherical cavity, thus decreasing the kinetic energy. This also results in a large increase in the Coulomb repulsion as the electrons now occupy the same cavity. The solvent potential is apparently not strong enough to stabilize the zero-bond-length configuration and the electron distribution is forced to spring back to its original peanut shape. This behavior occurs on the ground-state surface and is not the result of the breakdown of the adiabatic approximation.

In Fig. 3 the time dependence of the electron distribution during a typical hopping event is shown. The distribution begins in a peanut-shaped cavity, jumps to a single cavity, and then rebounds to another peanut-shaped cavity rotated from the first. The jump events are not simply an oscillation, but lead to diffusion of the bipolaron through the fluid. Thus, the mechanism for bipolaronic motion in the fluid is not that of a rigid diatom but consists in part of leapfrog hopping events. To quantify this statement, the diffusion coefficient of the average spin-up position, the average spin-down position, and the average positions of the total density and the solvent were calcu-

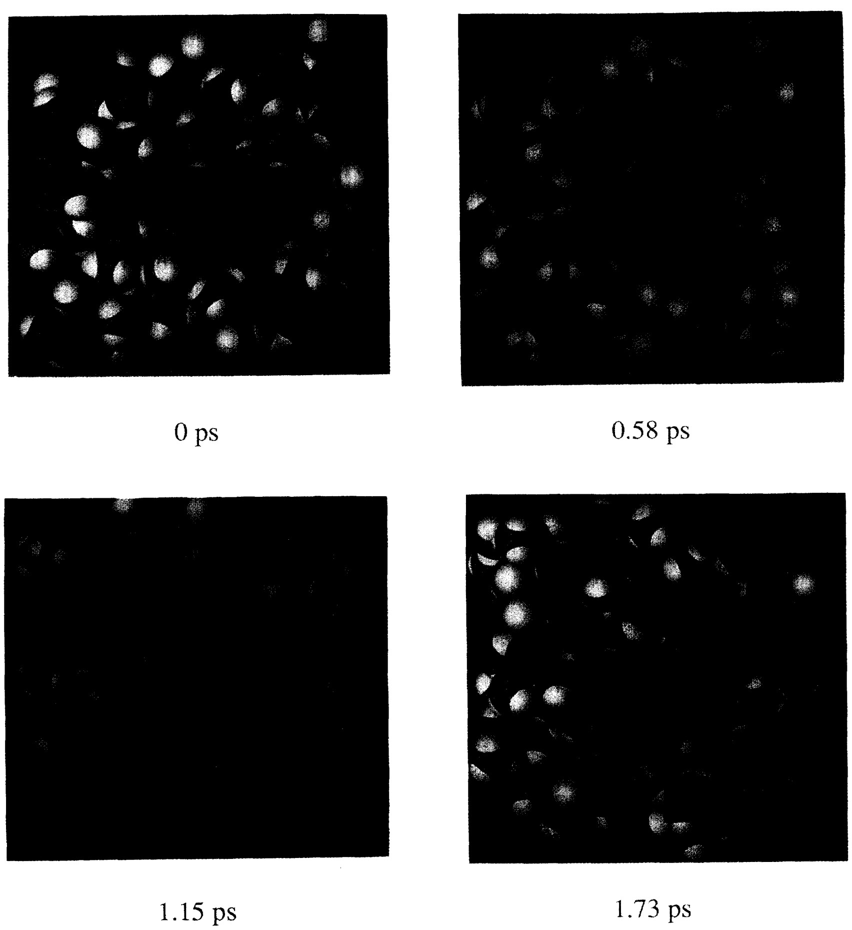


FIG. 3. The time evolution of a hopping event for a singlet-state bipolaron in liquid ammonia. The interval between each snapshot is 0.6 ps.

lated. The spin-up and spin-down positions have a diffusion coefficient of 1.2 $Å^2$/ps, while the average position of the density has a diffusion coefficient of 0.8 $Å^2$/ps. The solvent has a diffusion coefficient of 0.7 $Å^2$/ps, a value which is essentially that of a single excess electron in our model. Thus, the calculated value of the diffusion constant of the single excess electron is about 2 times smaller than experiment. It can therefore be seen that the bipolaronic hopping events give a reasonably large contribution to the diffusion coefficient in our model.

The time between hopping events and the rather unique diffusive behavior of the bipolaron leads to some interesting questions about the nature of the electron-solvent coupling that leads to the hops. That the electrons do not return to the same cavity suggests that they likely couple to shear modes of the ammonia fluid. Indeed, the time scale (5 ps) of the events is longer than the period of the smallest longitudinal solvent mode in the system (256 solvent molecules).

In summary, Car-Parrinello calculations have been performed for singlet-state and triplet-state bipolarons in liquid ammonia at an electron density where spin pairing is dominant but the system is not yet metallic, i.e., at ~ 1 MPE. In the singlet state, the electrons are found to occupy a peanut-shaped cavity with the peaks in the distribution separated by 7 Å, while in the triplet state the electrons dissociate. The binding energy of the singlet state is found to be 0.6 eV relative to the triplet and 0.3 eV relative to two isolated electrons at infinite dilution. This is precisely the behavior postulated by Mott [5] for metal ammonia solution at this density. In addition, a detailed study of the dynamics of the system has revealed a novel mechanism for bipolaronic diffusion. The electrons hop from peanut-shaped cavities to spherical cavities back to another peanut-shaped cavity in different regions of the fluid. This leapfroglike behavior was quite unexpected and may be relevant to other systems exhibiting transport of spin-paired species.

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[1] J. C. Thompson, *Electrons in Liquid Ammonia* (Oxford Univ. Press, London, 1976).

[2] *Physics and Chemistry of Electrons and Ions in Condensed Matter*, edited by J. Acrivos (Reidel, New York, 1984).

[3] M. Sprik, R. W. Impey, and M. L. Klein, Phys. Rev. Lett. **56**, 2326 (1986).

[4] M. Marchi, M. Sprik, and M. L. Klein, J. Phys. C **2**, 5833 (1990).

[5] N. F. Mott, *Metal-Insulator Transition* (Barnes and Noble, New York, 1974).

[6] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[7] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[8] E. Fois, A. Selloni, and M. Parrinello, Phys. Rev. B **39**, 4812 (1989).

[9] E. Fois, A. Selloni, M. Parrinello, and R. Car, J. Phys. Chem. **92**, 3268 (1988).

[10] F. Leclerq, P. Damay, and P. Chieux, Collque Weyl VII report, 1991 (to be published).

[11] R. Impey, M. Sprik, and M. L. Klein, J. Am. Chem. Soc. **109**, 5900 (1987).

[12] G. Martyna and M. L. Klein, J. Phys. Chem. **95**, 515 (1991).

[13] G. Martyna and M. L. Klein, J. Chem. Phys. (to be published).

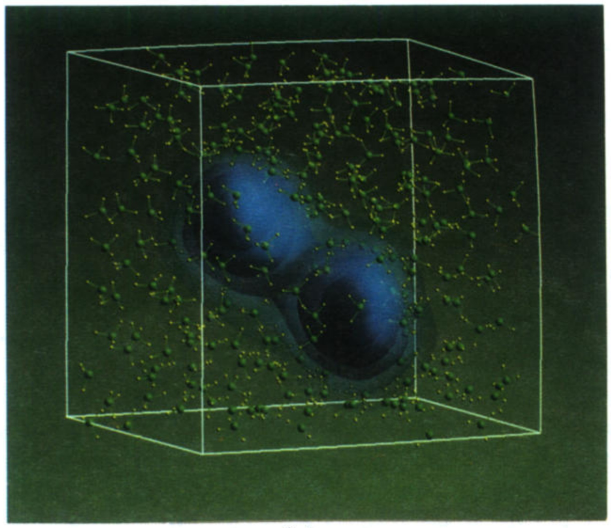
[14] *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).

[15] D. K. Remler and P. A. Madden, Mol. Phys. **70**, 921 (1990).

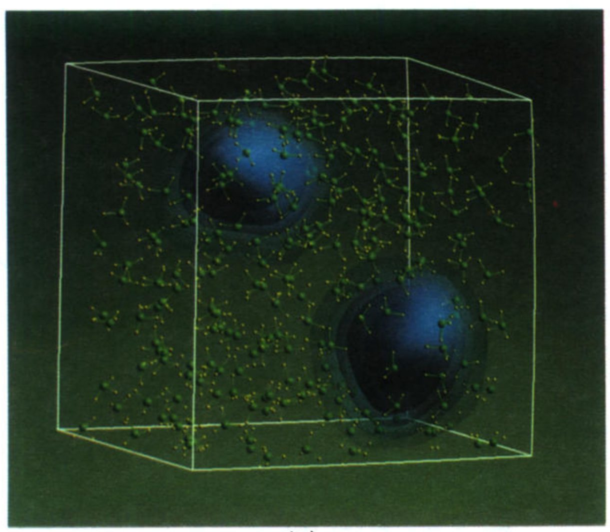
[16] M. Sprik, J. Phys. Chem. **95**, 2283 (1991).

[17] G. Martyna, Z. Deng, and M. L. Klein (to be published).

[18] J. J. Lagowski and M. J. Sienko, *Metal-Ammonia Solutions* (Butterworths, London, 1969).



(a)



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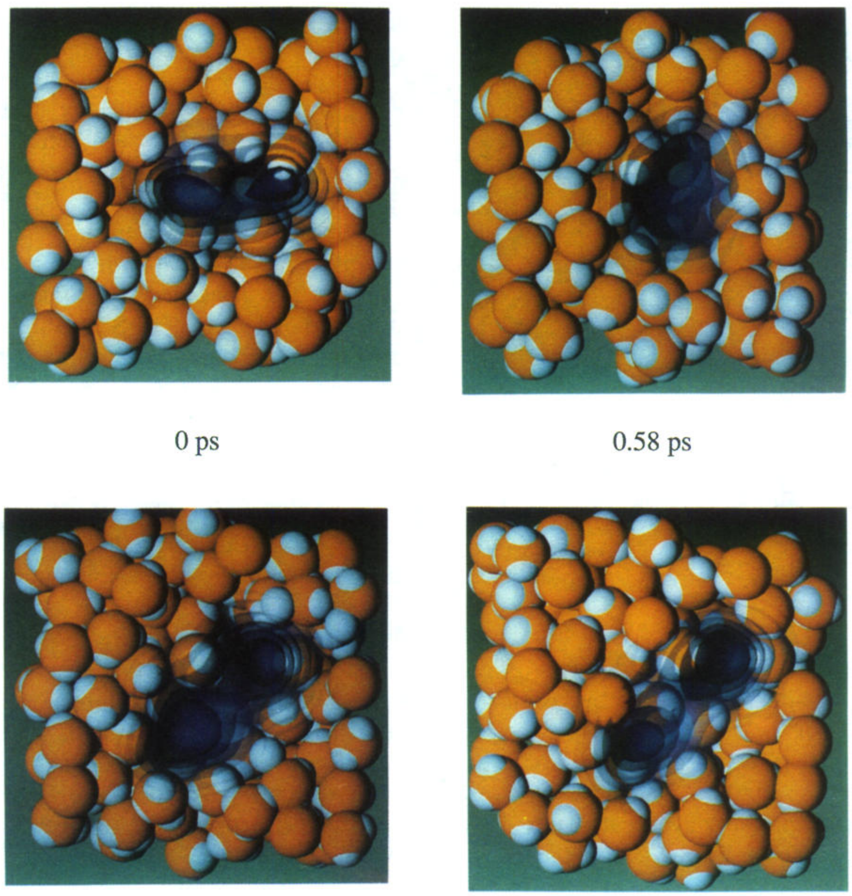

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