

G. N. Lewis' Atom and Quantum Monte Carlo Studies of Liquids

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Liquids that involve changes in electronic structure are difficult to simulate using pairwise additive forces. In this paper we use a semiempirical model of the internal structure of atoms in order to simulate simultaneously electronic and nuclear dynamics of fluids. The proposed excitonic phase of mercury is critically examined with these models.

KEY WORDS: Quantum Monte Carlo; path integrals; excitonic fluids; lattice fermions.

1. INTRODUCTION

The Monte Carlo method pioneered by Metropolis and co-workers⁽¹⁾ at Los Alamos has played a revolutionary role in changing the rules of argument in liquid state physics. Before the introduction of the Monte Carlo method and its sister, molecular dynamics,⁽²⁾ liquid state theory consisted of either austere mathematical formalism (e.g., the integral equation approach⁽³⁾) or unbridled but picturesque scenario building (e.g., Eyring's significant structure theory⁽⁴⁾). Both of these latter approaches can still be useful because they provide simple ways of thinking about complex problems. Nevertheless, the Monte Carlo method provided rich data sets that allowed fundamental tests of these ways of thinking. One could not blame the lack of agreement of a theory with Monte Carlo on errors in potential energy functions. Some theories were discarded and new ones introduced. The discipline provided by these computer experiments, instead of killing the field, led to a flowering of new and (perhaps) correct ideas.

There are areas of liquid state theory (and chemical physics, in general) which have been relatively untouched by this revolution. Because

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the usual simulation approach is founded on the idea of a simple potential energy function, there has been little work on simulating systems in which the electronic structure changes substantially with nuclear rearrangement. Thus, molecular fluids are well-understood, but systems such as liquid and amorphous semiconductors, electrons in polar fluids, and expanded fluid metals are still areas for relatively undisciplined speculation. Perhaps more importantly, any problem in chemistry in which bonds are made or broken is still difficult to approach in the condensed phase. Clearly, to go beyond this stage one must simulate the electronic and nuclear motion simultaneously. This immediately immerses the simulator in quantum mechanics, a sometimes unfamiliar territory.

Recently, several approaches to this simulation problem have been developed. One powerful approach is entirely *ab initio*.⁽⁵⁾ Using the Green's function Monte Carlo scheme, Alder, Ceperley, and co-workers have simulated many of the condensed phases of hydrogen. This method, at least superficially, appears to scale up only with difficulty to higher Z elements. Thus, impatient investigators are tempted to invent semiempirical models to simulate more complex systems. Such models, of course, are not guaranteed to simulate actual systems, but we should remember Lennard-Jonesium is not real argon. The study of semiempirical quantum models can act to discipline analytic theory and scenario-building in the same way as the early classical Monte Carlo studies of liquids disciplined liquid theory.

One kind of semiempirical approach, the pseudopotential, is based on a single particle picture of the electronic structure. This model is quite appropriate for systems such as the solvated electron which has been much discussed at this meeting.⁽⁶⁾ The pseudopotential picture⁽⁷⁾ is easy to interface with path integral quantum mechanics. The path integral quantum mechanism can be implemented in a Monte Carlo procedure by utilizing the isomorphism with polymer statistical mechanics.⁽⁸⁾ Other one-electron problems can be approached in this way also. At Illinois we are using it to study electron tunneling in proteins.⁽⁹⁾

Another semiempirical approach is the use of $X\alpha$ or density functional theories to calculate energies in a Monte Carlo run. Here the electron's dynamics is done by an extension of standard quantum chemical theory. Car and Parrinello⁽¹⁰⁾ have begun to use this approach for amorphous silicon. Because the underlying quantum chemical theory ignores important correlation effects, situations in which bonds are made or broken may not be treated well. Further experience may show this kind of problem not to be fatal.

We want to describe another semiempirical approach in this article. The model is motivated as much by ease of simulation as by fidelity to

nature (although we do feel it is not bad in this respect). Lattice models have been used extensively in quantum Monte Carlo studies in particle physics.⁽¹¹⁾ Piech and Wilson⁽¹²⁾ introduced similar models for atoms but this development had not been extensively followed up. It turns out this model is very reminiscent of early twentieth century atomic models of G. N. Lewis, and we illustrate in this paper how they may be used to simulate electronic state dynamics in liquids. The particular system that we chose to model is expanded-fluid mercury. This system was chosen because it seems to have an unusual phase transition in which electronic dynamics is important.⁽¹³⁾

The organization of the paper is as follows. We first discuss the lattice atom model and how Monte Carlo can be used to simulate it. Second, we discuss the puzzling phenomena in expanded mercury and one scenario for the transition according to Turkevich and Cohen.⁽¹⁴⁾ Third, we show how the simulations relate to this scenario.

2. THE LATTICE ATOM AND PATH INTEGRAL MONTE CARLO

One of the crucial early ideas in structural chemistry is the notion of directed bonds. A good zeroth order understanding of organic chemistry comes thinking of electrons in a saturated carbon atom as sitting at the corners of a tetrahedron, each one capable of forming a bond. We now know this is due to the sp^3 hybridization of the atom caused by its interaction with bonding partners. We usually think of the hybridization as changing when the neighbors change (e.g., in unsaturated hydrocarbons the hybridization is sp^2) although other descriptions such as bent or banana bonds have also been postulated.

Because of this important feature of directionality (and some other things such as the octet rule) G. N. Lewis postulated a lattice model of the electronic structure of the atom in 1923.⁽¹⁵⁾ A picture from his notebook is reproduced in Fig. 1. The Lewis model was a classical one; the electrons essentially sit at the lattice sites.

The quantum mechanical extension of the Lewis model is not difficult to imagine. One must allow transfer of the electrons from site to site. This is exactly what was done by Piech and Wilson.⁽¹²⁾ In second quantized notation their Hamiltonian for an isolated atom is

$$H = \sum_n \left\{ A_n \psi_n^+ \psi_n + \sum_m V_{nm} \psi_m^+ \psi_n^+ \psi_m \psi_n + t \sum_m (\psi_m^+ \psi_n + \psi_n^+ \psi_m) \right\} \quad (1)$$

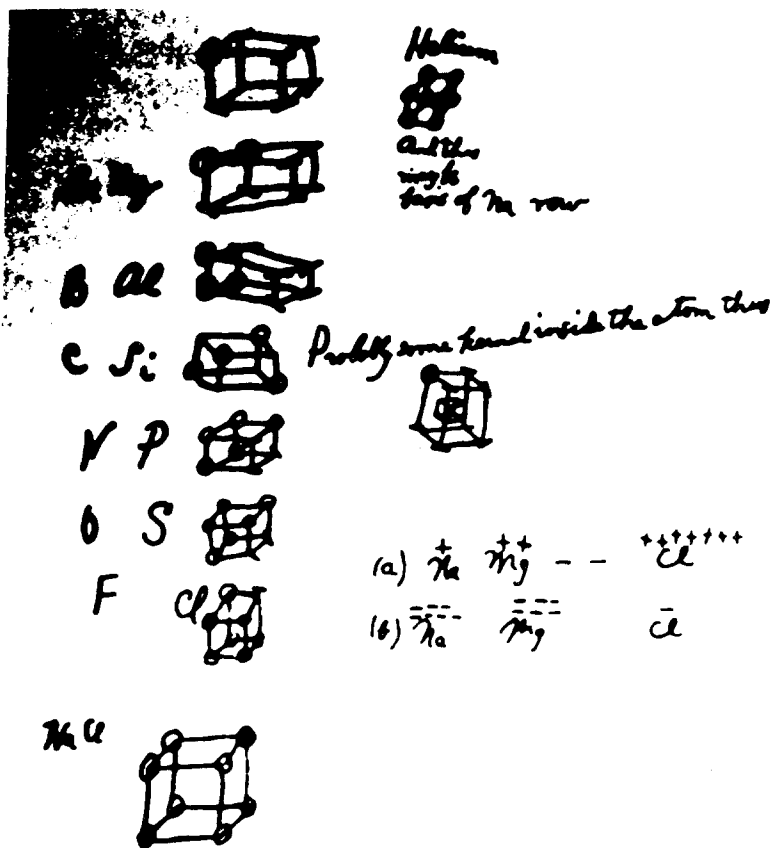


Fig. 1. A page from G. N. Lewis' notebook showing his lattice models of atoms. This is reproduced from Ref. 15.

ψ_n^+ is the creation operator for an electron on a site, ψ_n is the annihilation operator, t is the transfer matrix element, V_{nm} the electron interaction term, and A_n the site energy. (A semiempirical model would treat only the valence electrons with renormalized matrix elements.)

Let us now imagine a single valence electron atom. If the atom is isolated it will transfer between all the sites, thereby blurring out to have nearly spherical (cubic) symmetry. In the presence of an external field it will spend more time on one of the sites than the others. It will have hybridized into a directional orbital.

How do we use this picture for a many-atom system? Ideally one should allow the electrons to hop from atom to atom and retain the direct electron-electron Coulomb interactions. For an arbitrary nuclear con-

figuration the system then is like a random lattice fermion model,⁽¹⁶⁾ with all of its concomitant difficulties. For some problems we can suppress the interatom electron hopping. When hopping occurs an ionic configuration is transiently formed. This is higher in energy than the neutral configurations. We should bear in mind that condensed phase effects can make ionic configurations more favorable, but our models will not deal with this. If the ionic configurations are projected out, one is left with new effective interaction between electrons on different atoms. This is the weak exchange limit of the chemical bond.⁽¹⁷⁾ Thus we take the electron–electron interactions between different atoms as an adjustable function, much like the intermolecular potential in a conventional simulation. With the suppression of interatom hopping the usual fermionic difficulties are ameliorated—for one and two electron atoms in singlet states they are eliminated.

In the model problem that we have chosen to study the mercury atom behaves as a one-electron atom. This is because the physics of mercury–mercury interactions is thought to arise from single particle excitation on each atom. When an electron sits on a lattice site the atom has a dipole. These dipoles then interact through electrostatic potentials. Thus our Hamiltonian is a simplified version of (1). The Hamiltonian can be written as

$$H = \sum_i H_{el}^{(0)}(\mu_i) - \sum_{i < j} \boldsymbol{\mu}_i \cdot T_{ij} \cdot \boldsymbol{\mu}_j + \sum_{i < j} u_o(\mathbf{r}_i, \mathbf{r}_j)$$

We have allowed the instantaneous dipole of the atom to be given by discrete values in which the dipole is pointed at the vertices of a cube centered on the atom. These values are labeled by the set $\{\boldsymbol{\mu}_i\}$ for each atom; $H_{el}^{(0)}$ is the internal electronic Hamiltonian which allows transitions between different $\{\boldsymbol{\mu}_i\}$ states, with matrix elements $t_{ij} = -\omega_o/2$ if i and j are nearest neighbors and 0 otherwise. ω_o is the atomic excitation frequency. The valence electrons interact through the dipole–dipole potential $-\boldsymbol{\mu}_i \cdot T_{ij} \cdot \boldsymbol{\mu}_j$. The core electrons provide a repulsive core which we model by a hard-sphere potential $u_o(\mathbf{r}_i, \mathbf{r}_j)$.

To carry out the simulation we treat the nuclei classically but the electrons' dynamics must be treated quantum mechanically. This is allowed because of the Born–Oppenheimer approximation. To treat both electrons and nuclei on the same footing we use path integral techniques.⁽⁸⁾ We find the equilibrium properties of this model from the P -point discretized path integral representation of the partition function, $Z = \text{tr}\{e^{-\beta H}\} = \text{tr}\{(e^{-\beta H/P})^P\}$. In this isomorphism the internal state of the lattice atoms is represented by a ring of P instantaneous moment positions $(\boldsymbol{\mu}^{(1)}, \boldsymbol{\mu}^{(2)}, \dots, \boldsymbol{\mu}^{(P)})$. The resulting approximate partition function is

$$\langle \boldsymbol{\mu}_N, \mathbf{r}_N | e^{-\varepsilon H} | \boldsymbol{\mu}'_N, \mathbf{r}'_N \rangle \propto \left[\prod_{k=1}^N \delta(\mathbf{r}_k - \mathbf{r}'_k) \right] e^{-\varepsilon \sum_{i < j} u_0(\mathbf{r}_i, \mathbf{r}_j) - \varepsilon \Phi}$$

$$\Phi = \sum_{i=1}^N \frac{(\boldsymbol{\mu}_i - \boldsymbol{\mu}'_i)^2}{4\varepsilon |\boldsymbol{\mu}|^2} \ln \left(\frac{1 + \Delta}{1 - \Delta} \right)$$

$$- \frac{1}{2} \sum_{i < j} \{ \boldsymbol{\mu}_i \cdot \mathbf{T}_{ij} \cdot \boldsymbol{\mu}_j + \boldsymbol{\mu}'_i \cdot \mathbf{T}_{ij} \cdot \boldsymbol{\mu}'_j \}$$

where $\Delta = \exp[-\varepsilon \omega_o]$.

$$Z_p = \int d\mathbf{R}_N \sum_{\{\boldsymbol{\mu}^\alpha\}} e^{-\beta \sum_{i < j} u_0(\mathbf{r}_i, \mathbf{r}_j)} \prod_{\alpha=1}^P e^{-\beta \Phi(\boldsymbol{\mu}^\alpha, \boldsymbol{\mu}^{\alpha+1})/P} \quad (2)$$

Because H_o does not commute with the interaction this expression is exact only as $P \rightarrow \infty$. In fact we find that $P = 150$ is sufficient for roughly 5% accuracy in binding energies. Even though only classical quantities are involved in (2), Z_p cannot be evaluated exactly for the many-particle system. The probability distribution for dipole moments and configurations can, however, be sampled via standard Metropolis Monte Carlo methods.

The Monte Carlo evaluation of the path integral sum is essentially calculating a fully correlated, highly nonadditive potential function for each nuclear configuration. In addition we can find out directly about the static electronic structure and limited time-dependent information from the imaginary-time dipole-dipole correlation function.

3. PUZZLES OF EXPANDED FLUID MERCURY

Under ordinary conditions mercury is a metallic liquid. Dilute gaseous mercury, however, is an insulator. One of the oldest questions that is still unresolved is, what is the relationship between the liquid-gas transition and the metal-insulator transition? One of the problems in understanding this is that the interatomic interactions are very different in the two states. In the dilute gas the mercury atoms are merely highly polarizable atoms interacting through weak Van der Waals interactions. In the liquid the valence electrons are "disassociated" and are thought to provide cohesive energy through their attraction with the positive ionic cores.⁽¹⁸⁾

Despite the difficulty of dealing with high pressure and high temperature corrosive fluids, numerous experimental studies of expanded fluid metals have been carried out with the goal of understanding these questions.^(13,19) One of the most important probes is the measurement of dielectric constants. The static dielectric constant of a metal is infinite, while for an insulator it is finite. In addition, one of the oldest theories of

the metal-insulator transition identifies the transition with dielectric instability of a model of interacting Drude model atoms. In this theory of Herzfeld's⁽²⁰⁾ the valence electrons are held by harmonic restoring forces to their respective nuclei in the insulator. When immersed in a polarizable medium, the restoring force is reduced by the reaction field from the surrounding medium. This increases the polarizability self-consistently. Eventually a catastrophe ensues.

When the dielectric measurements were carried out at Marburg⁽¹³⁾ an anomaly was discovered. At low density the dielectric constant obeyed the Clausius-Mossotti relation. However at 1800K and density $\rho \approx 3.3 \text{ g/cm}^3$, the dielectric constant shot up from values of around 2 to values around 10-20. Many scenarios for this behavior have been put forward.¹⁴ For a review, see Ref. 19. Although the conductivity does not change much, self-trapped negative ion states have been proposed.⁽²¹⁾ Because of the nearness to the critical point, another possibility might be some peculiar critical phenomena. Wetting has been proposed as an explanation.⁽²²⁾ Another possibility is conduction along giant metallic clusters.

One of the most exciting possibilities is that this is an example of an excitonic phase. Such phases in which excitons condense into a macroscopically occupied state were first postulated by Kohn⁽²³⁾ as intermediate phases in the metal-insulator transition. Turkevich and Cohen⁽¹⁴⁾ have explained the dielectric anomaly by assuming that it is such an excitonic transition which is seen. Their scenario is consistent with a large number of related observations about the mercury phase diagram.

The physical nature of the excitonic transition is easiest to understand in a localized picture of the excitons. We use the Frenkel rather than Wannier picture. A single mercury atom has a 1S ground state. It has both triplet and singlet excited states with P symmetry at energies of 4.9 and 6.7 eV higher, respectively. There is a large transition dipole, oscillator strength $f = 1.184$, connecting the ground and excited singlet states. This is responsible for the intense emission in mercury vapor lamps. If the mercury atom is in a state which is a superposition of the two states (that is, if the mercury atom changes hybridization), it then achieves a large dipole moment. This large dipole moment can then polarize its neighboring atoms. The resulting reaction field enhances the polarizability of the atom just as in the Herzfeld scenario for the metal-insulator transition. If there are a sufficient number of neighbors, the reaction field can overcome the energy cost of rehybridizing the atom entirely, and an effectively dipolar mercury atom would result. In a Drude atom the electron could dissociate, but this is impossible without more states. In this way the dielectric constant of the mercury would be greatly enhanced. In the Turkevich-Cohen scenario the dipoles then align and the material is ferroelectric. A smaller

enhancement of the dielectric constant would arise even if the stabilized dipoles did not align but remained pinned to a local frame determined by the instantaneous atomic positions. This would be a paraelectric (or equivalently, a quantum pseudo-spin glass phase in which the "spins" are electric dipole moments).

When mercury atoms rehybridize, their effective interactions change. The permanently dipolar atoms bind much more strongly. A similar situation has been found by Dykstra in magnesium clusters.⁽²⁴⁾ Using ab initio methods Dykstra has shown that Mg_2 is a weakly bonded van der Waals molecule. On the other hand, Mg_4 is a strongly bonded molecule. The binding energy comes from a correlation effect which involves S to P excitation as is envisioned in the excitonic model of mercury. The analogy is further plausible because of the similarity of the valence configuration of Hg and Mg.⁽²⁵⁾

The clustering that is concomitant upon rehybridization is an essential element of the Turkevich–Cohen scenario. Clusters of mercury atoms also figure in Bhatt and Rice's⁽²⁶⁾ treatment of the dielectric properties of mercury.

It is clear that the essential elements of the Turkevich–Cohen scenario are contained in a one-electron per atom, lattice atom model as discussed in the last section. We therefore proceed to simulate it.

4. COMPUTATIONAL DETAILS AND RESULTS

The calculations were carried out on an FPS 164 Array processor. Due to computational limitations these exploratory studies used only 32 atoms in a periodic box with a hard sphere radius of 5.059 Å and a temperature of 1800° K. Since there are ($P=$) 150 time slices on each atom, there are a total of ~ 4800 degrees of freedom. The long range of the dipolar interaction necessitated the use of Ewald summation⁽²⁷⁾ with the outer dielectric chosen to be $\epsilon = \infty$. We chose this outer dielectric constant because we did not want to bias the situation against a ferroelectric transition. If more particles were used one would expect the choice of outer boundary conditions not to be crucial.

We carried out two kinds of simulations, quenched and annealed averages. In an annealed run we let the centers of mass of the atoms readjust as we change the electronic states. For the quenched averages we sample a hard sphere configuration, hold this fixed, and then carry out a Monte Carlo sampling of the electronic paths. We allow these samples to equilibrate vis à vis electronic structure, gather statistics, and then choose new hard-sphere configurations. Comparison of these two kinds allows us

to study the importance of clustering in giving the observed behavior. Also, several analytic theories suppress clustering, so we wanted to test separately the merits of the other approximations made by these theories.

We calculated several quantities to get ideas about the transition. The experimental observable is the dielectric constant. Unfortunately, even for classical systems this is a tricky quantity to get right.⁽²⁷⁾ However, with our boundary conditions the dielectric constant of the sample can be obtained from the total moment fluctuations.

$$\varepsilon = 1 + \chi(0) = 1 + \int_0^\beta d\tau \langle \mathbf{M}(0) \cdot \mathbf{M}(\tau) \rangle d\tau$$

where \mathbf{M} is the total dipole moment at "time" τ . The integral over imaginary time is the Kubo transform, which, for quantum systems, is needed in order to write equilibrium response in terms of correlation functions.

We also calculated the single-particle dipole correlation function $\langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(\beta') \rangle$; it is this quantity which comes out most easily from analytic treatments of the transition. A pioneering description of the dielectric anomaly in terms of the mean spherical approximation (MSA) was put forward by Logan and Edward.⁽²⁸⁾ Their theory was based on many studies of this venerable approximation.⁽²⁹⁾ The explicit calculations of Logan and Edwards were based on the Drude oscillator (harmonic atom) model *not* the lattice atom model. Thus, the comparison of MSA results tells us about some of the effects of the detailed level structure—the Drude oscillator having many more excited states than the 1P considered in the Turkevich–Cohen scenario. Their work gives the remarkable prediction that expanded fluid lithium should also exhibit such an anomaly.

Two aspects of the dipole correlations are most significant. One is its imaginary-time integral $\alpha(0) = \frac{1}{3} \int_0^\beta d\tau \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(\tau) \rangle$. This is just the static susceptibility. The other quantity

$$q = \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(\beta) \rangle / \mu^2$$

tells us whether permanent dipoles have formed. If only a small amount of rehybridization exists, q should essentially vanish. q is a little like a spin glass order parameter because it is the "long" time limit of the time-correlation function. Another derived quantity is $f = q^{1/2} / \langle |\mathbf{M}| / N \rangle$. If $f > 1$, the new permanent moments have not mutually aligned to any extent; if $f \approx 1$ the configuration is clearly ferroelectric.

In addition to these quantitative measures we examined snapshots of configurations in the system. These give one clear impressions about the extent of clustering in the model. By representing the average dipole on

these atoms as well (this is roughly the same as $q^{1/2}$), one gets a feeling for the degree of rehybridization.

The MSA-Drude calculation could explain the anomaly with a bare mercury polarizability $\alpha_o \approx 45au^3$. We thus did extensive studies with this value. The results for the renormalized polarizability $\alpha(0)$ are shown in Fig. 2. The quenched runs are indicated by circles, the annealed with triangles. Also indicated are several analytic approximation based on the MSA and its extensions; the top solid line is the MSA-Drude result. All the analytic results have been corrected for finite size effects inherent in our 32-

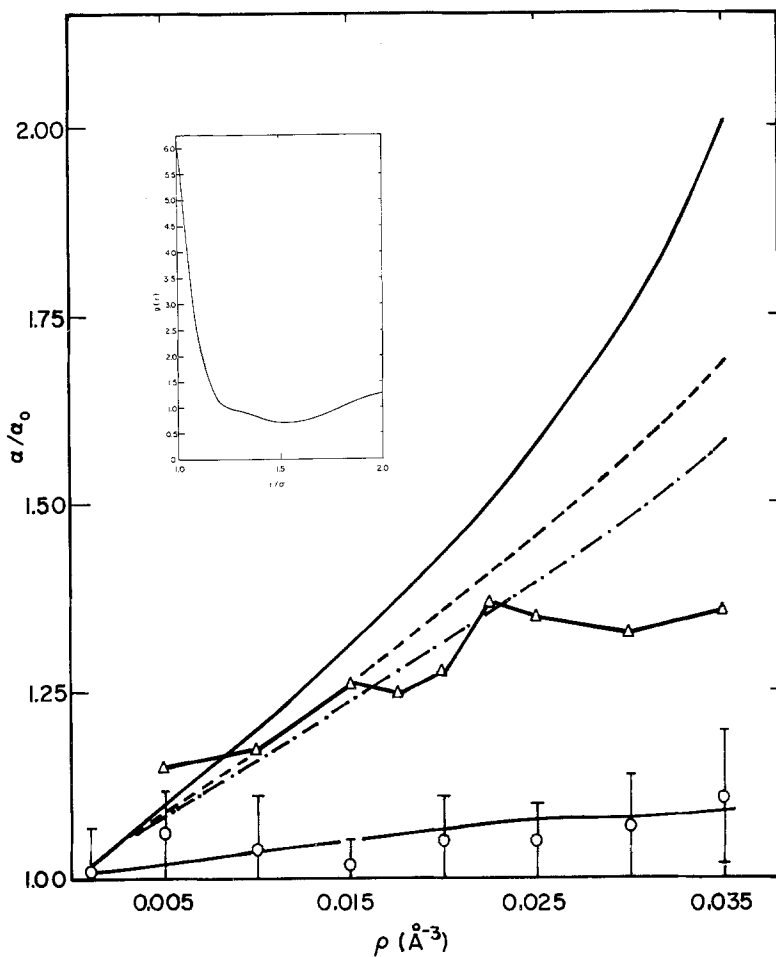


Fig. 2. The renormalized polarizability of the model fluid. In the inset is shown the pair-correlation function at a density of $.015 \text{ \AA}^{-3}$ and $\alpha_o = 45au^3$.

particle Ewald summed system. The MSA-Drude does not do too badly at imitating the annealed results. However, this is fortuitous. Since the MSA assumes no clustering it should be compared with quenched results. The discrepancy is due to the finite level structure of the lattice atom. When we use the optimized random phase approximation (ORPA),⁽³⁰⁾ which is an extension taking into account the finite level scheme, agreement is excellent, as is indicated by the lower solid line in Fig. 2. Thus, this example shows the power of Monte Carlo; it can reveal the presence of cancelling approximations in analytic theories.

Because ORPA was found to be reliable for quenched systems, we used this to guide our studies. For the lattice atom the excitonic transition does not occur at $\alpha_o = 45au^3$ for quenched configurations. The ORPA suggested a transition at $\alpha_o \approx 125au^3$ and $\rho = .012\text{\AA}^{-3}$. Simulations confirmed this.

In Table I we summarize our runs vis-a-vis our quantitative measures

Table I. $\alpha(o)/\alpha_o$, q , ϵ , and f as a Function of Density and α_o ^a

ρ	α_o	$\alpha(o)/\alpha_o$	q	ϵ	f
.001	45	1.01(.06)	-.003(.010)	1.03(.01)	0
.005		1.06(.06)	.001(.006)	1.15(.03)	0
.010		1.04(.07)	.003(.008)	1.22(.060)	0
.015		1.02(.03)	-.004(.009)	1.56(.14)	0
.020		1.05(.05)	.002(.011)	1.36(.04)	0
.025		1.05(.05)	.000(.008)	1.65(.12)	0
.030		1.07(.07)	.000(.010)	2.20(.23)	0
.035		1.11(.09)	.003(.009)	2.53(.22)	0
.005	45	1.15(.09)	-.003(.013)	1.53(.03)	0
.010		1.16(.09)	.000(.011)	3.03(.62)	0
.015		1.27	.003	3.43(.29)	0
.020		1.34	.0000	4.83(.35)	0
.025		1.35	-.003	8.82(.72)	0
.030		1.33	-.001	9.21(1.33)	0
.035		1.40	.004	15.5(1.34)	0
.0075	125	1.23(.15)	-.002(.015)	2.63(.37)	0.0
.010		1.25(.17)	-.002(.020)	4.16(.49)	0.0
.011		1.31(.18)	-.019(.024)	4.00(.41)	0.0
.0125		2.74(.38)	.065(.026)	21.64(2.47)	1.7
.015		3.65(.47)	.107(.032)	20.30(1.70)	2.4
.020		5.66(.44)	.202(.031)	20.29(1.78)	1.2

^a q , ϵ , and f are defined in the text. Errors are indicated in parenthesis. The first two sets of numbers use hard sphere nuclear configurations, the last set was obtained allowing the nuclei to move. ρ is in units of \AA^{-3} , and α_o is in units of au^3 .

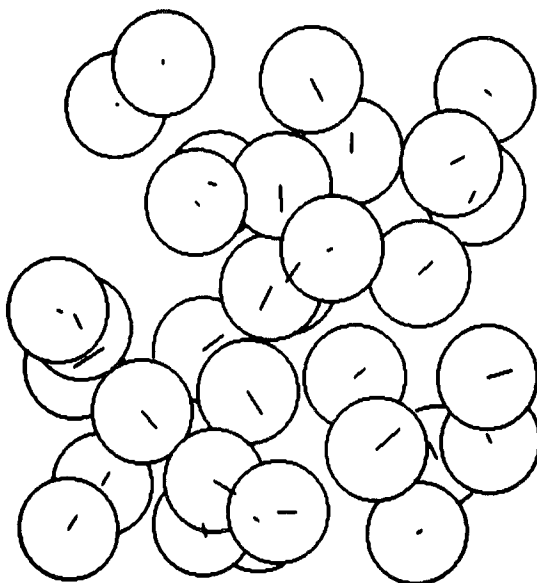


Fig. 3. A snapshot from the Monte Carlo run at $\rho = .015 \text{ \AA}^{-3}$ and $\alpha_o = 125au^3$. The length of the lines in the atoms indicates the size of the time-averaged dipole moment.

$\alpha(0)$, q , ε , and f . The quenched $\alpha_o = 45au^3$ runs just discussed do not show a transition. The last set of $\alpha_o = 125au^3$ runs show a marked transition. q takes a large jump at $\rho \sim .0125 \text{ \AA}^{-3}$ and ε jumps from 4 to approximately 20. The f value shows alignment but is rather noisy and only at the highest density is the system clearly ferroelectric. Snapshots clearly show the alignment (see Fig. 3).

What of the annealed runs? The $\alpha_o = 45au^3$ runs do not show an excitonic transition. They do, however, exhibit clustering as exhibited in the pair-distribution function (see inset of Fig. 2.) There is also an enhancement of ε due to clustering, but this is not nearly so rapid as at an excitonic transition. If we use $\alpha_o = 150au^3$ the excitonic transition does occur, but now the intermolecular forces are so strong that clustering takes place with a vengeance. In fact, solidification ensues with the system collapsing into a crystalline cluster. Thus our model does have the possibility of exhibiting an excitonic transition, but apparently not in the fluid state. This point cannot be made too dogmatically, however, since we have not done a full parametric search, and the balancing of these two transitions may be delicate. (An intermediate value of α just might bring the balancing act off.)

5. DISCUSSION

Our lattice atom model of expanded fluid mercury has not settled the experimental puzzles. One nice aspect of our study is that it does show the subtleties that can arise from coupled quantum phase transitions. This subtlety is not fully appreciated in other attempts. Another feature which our study illustrates is how Monte Carlo, when combined with analytic theory and qualitative ideas, can allow us to dissect a phenomenon and learn about the adequacy of various approximations made in theories and models.

Clearly much more elaborate models can and must be developed. The role of the triplet excitations must be explored. The sensitivity to the core potential and assumptions about the electron-electron interaction must be addressed. Models which allow a true metal-insulator transition should also be examined.

Whole families of models along these lines can be investigated. We anticipate that their investigation will be fun and, hopefully, enlightening.

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REFERENCES

1. N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.* **21**:1087 (1953).
2. B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* **27**:1208 (1970); B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* **31**:459 (1959).
3. H. L. Frisch and J. L. Lebowitz, eds. *The Equilibrium Theory of Classical Fluids*, eds. (Benjamin, New York, 1964).
4. M. S. John and H. Eyring, in *Physical Chemistry, an Advanced Treatise*, vol. VIII A, H. Eyring, D. Henderson, W. Jost, eds. (Academic Press, London, 1971), p. 335.
5. M. H. Kalos, in *Monte Carlo Methods in Quantum Problems*, M. H. Kalos, ed. (Reidel, Dordrecht, 1984) p. 19; D. Ceperley, *ibid*, p. 47.
6. *J. Stat. Phys.* **43**(5/6) (1986).
7. J. D. Weeks, A. Hazi, and S. A. Rice, *Ad Chem. Phys.* **16**:282 (1969).
8. D. Chandler and P. G. Wolynes, *J. Chem. Phys.* **74**:4078 (1981).
9. A. Kuki and P. G. Wolynes, work in progress.
10. R. Car and M. Parrinello, preprint.
11. R. L. Sugar, in *Monte Carlo Methods in Quantum Problems*, M. H. Kalos, ed. (Reidel, Dordrecht, 1984) p. 157; J. E. Hirsch, *ibid*, p. 187.
12. K. R. Piech and K. G. Wilson, *J. Chem. Phys.* **48**:3740 (1968).

13. W. Hefner and F. Hensel, *Phys. Rev. Lett.* **48**:1026 (1982); W. Hefner, R. Schmutzler, and F. I. Hensel, *J. Phys. (Paris) Colloq.* **41**:C8-62 (1980).
14. L. A. Turkevich and M. H. Cohen, *Ber. Bunsenges Phys. Chem.* **88**:292 (1984); L. A. Turkevich and M. H. Cohen, *J. Phys. Chem.* **88**:3751 (1984).
15. G. N. Lewis, *Valence and the Structure of Atoms and Molecules* (The Chemical Catalog Company, New York, 1923), p. 29.
16. N. H. Christ, R. Friedber, and T. D. Lee, *Nucl. Phys. B.* **202**:89 (1982); *Nucl. Phys. B.* **210**:310 (1982); *Nucl. Phys. B.* **210**:337 (1982).
17. J. Friedel, in *Physics and Chemistry of Electrons and Ions in Condensed Matter*, J. V. Acrivos, ed. (Reidel, 1984) p. 45.
18. J. M. Ziman, *Models of Disorder* (Cambridge Press, Cambridge, 1979), Chap. 10.
19. *J. Phys. Chem.* **88** (1984).
20. K. F. Herzfeld, *Phys. Rev.* **29**:701 (1927); *J. Chem. Phys.* **44**:429 (1966).
21. J. P. Hernandez, *Phys. Rev. Lett.* **48**:1682 (1982); **44**:429 (1966); *J. Phys. Chem.* **16**:3465 (1983).
22. M. E. Fisher, private communication.
23. D. Jerome, T. M. Rice, and W. Kohn, *Phys. Rev.* **158**:462 (1967).
24. R. A. Chiles and C. E. Dykstra, *J. Chem. Phys.* **74**:4544 (1981); *J. Chem. Phys.* **75**:1044 (1981).
25. E. W. Smith, R. E. Drullinger, M. M. Hessel, and J. Cooper, *J. Chem. Phys.* **66**:5667 (1977); P. J. Hay, T. H. Dunning, Jr., and R. C. Raffanetti, *J. Chem. Phys.* **65**:2679 (1976); F. H. Mies, W. J. Stevens, and M. Krauss, *J. Molec. Spect.* **72**:303 (1978).
26. R. N. Bhatt and T. M. Rice, *Phys. Rev B* **20**:466 (1979).
27. S. W. deLeeuw, J. W. Perram, and E. R. Smith, *Proc. R. Soc. Lond. A* **373**:27 (1980).
28. D. E. Logan and P. P. Edwards, submitted to *Phil. Mag.*
29. J. S. Høye and G. Stell, *J. Chem. Phys.* **75**, 5123 (1981); M. J. Thompson, K. S. Schweizer, and D. Chandler, *J. Chem. Phys.* **76**:1128 (1982); D. Chandler, K. S. Schweizer, and P. G. Wolynes, *Phys. Rev. Lett.* **49**:1100 (1982).
30. E. C. Behrman, G. A. Jongeward, and P. G. Wolynes, *J. Chem. Phys.* **83**:668 (1985).