PHYSICAL REVIEW B **71**, 024204 (2005)

# Validation of a glue-model approach in a tight-binding hard-sphere model for hot fluid metals

E. Chacón,[1] M. Reinaldo-Falagán,[2] P. Tarazona,[2] E. Velasco,[2] and J. P. Hernandez[3]
[1]*Instituto de Ciencia de Materiales de Madrid, CSIC, E-28049 Madrid, Spain*
[2]*Física Teórica de la Materia Condensada (C-V) Universidad Autónoma de Madrid, E-28049 Madrid, Spain*
[3]*Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27599-3255, USA*

(Received 23 April 2004; revised manuscript received 8 September 2004; published 21 January 2005)

We have calculated thermodynamic, structural, and electronic properties of a model fluid of monovalent atoms which interact via hard-sphere repulsions and an attraction arising from the delocalization free energy of the valence electrons. These properties result from self-consistent Monte Carlo simulations of equilibrium ionic structures based, at each step in which an ion is to be moved, on the exact electronic free energies corresponding to the ionic configurations. The electronic energy is derived from a tight-binding model with electronic hopping which decays exponentially with distance. The liquid-vapor coexistence curve and both ionic and electronic structures are obtained. By direct comparisons, the present results confirm previous ones which were obtained basing the simulations on a glue-model description of ion energies. The importance of this confirmation is the validation of the glue-model approach, one of the few computational simplifications possible for realistic metallic fluids.

DOI: 10.1103/PhysRevB.71.024204 PACS number(s): 64.70.Fx, 61.25.Mv, 64.60.Cn, 71.22.+i

## I. INTRODUCTION

In recent work[1] we studied a conceptually simple model for a monovalent-atom fluid, one with ionic hard-sphere repulsions and electron hopping which plays a central role by providing the only system cohesion. Beyond any intrinsic interest, we sought a qualitative understanding of some experimentally observed alkali-fluid properties based on calculations with a tractable model. We were mainly concerned with two aspects of the system, the phase coexistence between a dense liquid metal and a nonmetallic molecular vapor and the electrical conductivity at near-coexistence conditions. In the model, as in the experimental cases, the electron-ion interaction induces correlations among the atomic positions, not describable via a pair potential, which dramatically influence the structural, thermodynamic, and electronic properties through the required self-consistency between ionic and electronic structures. As the previous work was based on a glue-model approximation to the electronic energies, in the present work we treat the energies exactly to reexamine the basis of the thermodynamic, structural, and electronic density of states results and thus validate our previous methods and conclusions.

Previous results were based on simulations with 1500 particles and more than $10^9$ Monte Carlo (MC) steps, they became feasible using a description of the attractive interactions using a sophisticated glue model. To validate that approach, we now recalculate the thermodynamic and structural properties on the basis of the exact system energies, albeit using a smaller system of particles. In the glue model, the energy of each atom is described as a parametrized functional of its local environment. The so-called glue methods have many different implementations and justifications: the embedded-atom method,[2] the effective-medium theory,[3] the second-moment approximation,[4] and others.[5] The reason for using a glue-model approach was that, even given the simplicity of our model, simulations of the structures, based on the exact energies, required a very high computational cost: the diagonalization of an $N \times N$ matrix at each step in the structural simulations. Spot checks, described in the previous publication, suggested that allowing the simulations to develop using the glue-model energies was an adequate procedure. We now report calculations of the coexistence conditions themselves, based on the exact energies and alternate simulation methods. The previously obtained thermodynamic and structural results are confirmed. The importance of this confirmation is that it validates the glue-model approach, one of the only computational simplifications possible for this type of problem. The results suggest the adequacy of such a glue-model approach which can make feasible the computational effort required for realistic treatments of hot metallic fluids.

Further, given the importance of electronic properties in metallic systems and their close relation to ionic structures, we have tested whether using the glue approximation substantially affects the calculated electronic properties of the system. In this paper, the test has consisted in comparing the electronic densities of states, at appropriate ionic densities and temperatures, obtained from using equilibrium ionic structures based on both the exact energies and the glue-model approximation. The electrical conductivity is naturally of interest and a broader topic. Given the complexity of the conductivity and the need to analyze its calculation in depth, we have chosen to treat it in a separate article;[6] that article presents a systematic study of methods and approximations used to obtain the electrical conductivity of hot metallic fluids, with the thermalized and highly disordered ionic structures described by the present model. Those comparisons also verify the adequacy of the glue model.

## II. TIGHT-BINDING HARD-SPHERE MODEL

For completeness, the model system is described in this section. Our approach is a self-consistent one in the treatment of ions and electrons. The ionic structures take into account hard-sphere (HS) interactions and the coupling with the free energy due to valence electron delocalization. This electronic energy is in principle dependent on all the ionic positions in each configuration and provides an effective attraction among ions. Given an ionic configuration, the electrons, one per ion, are described by a tight-binding (TB) model in which a single orbital is associated with each ion and coupled, via hopping matrix elements, to the orbitals at the other ionic sites. The Hamiltonian for the electrons is the following:

$$H = -\sum_{(i,j)s} t_{ij} c_{is}^{\dagger} c_{js}, \tag{1}$$

with $c_{is}$ ($c_{is}^{\dagger}$) being the annihilation (creation) operator for an electron, with spin $s$ at site $i$; the site energy is defined as zero and

$$t_{ij} \equiv t(r_{ij}) = t_0 \exp[-\alpha(r_{ij} - d_{\mathrm{HS}})], \tag{2}$$

where $r_{ij}$ is the distance between ions $i$ and $j$ and $d_{\mathrm{HS}}$ is the hard-sphere diameter. As the thermal energies of interest turn out to be comparable to the energy scale $t_0$, we require the Helmholtz free energy of the electrons described by the above Hamiltonian: $F_{\mathrm{el}} = \langle H \rangle - TS_{\mathrm{el}}$; the thermal average ($\langle \ldots \rangle$) and the electronic entropy are obtained using the Fermi-Dirac distribution function to occupy the available one-electron states $\epsilon_k$, with $k=1$ to $N$. An explicit expression for the Helmholtz free energy of the electrons, with the atoms in the configuration determined by the relative positions $r_{ij}$, can be written as

$$F_{\mathrm{el}} = -\mu N - (2/\beta) \sum_{k=1}^{N} \ln[\exp\{\beta(\epsilon_k - \mu)\} + 1], \tag{3}$$

with $\beta = 1/k_B T$ and $\mu$ being the electronic chemical potential, which statistically guarantees that there are $N/2$ electrons of each spin. Clearly, this free energy depends on the ionic configuration through the $t_{ij}$ dependence of the one-electron energies. We close the self-consistency, within the model, by requiring thermal equilibrium for the ionic distributions: taking $F_{\mathrm{el}}$ as the only cohesive energy for nonoverlapping ions in any possible configuration.

Reduced units in terms of the contact hopping $t_0$ and the HS diameter $d_{\mathrm{HS}}$ will be used for temperature $T^* = k_B T / t_0$, density $\rho^* = \rho d_{HS}^3$, and the exponential decay of the hopping $\alpha^* = \alpha d_{\mathrm{HS}}$. For computational efficiency $F_{\mathrm{el}}$, in the previous work, used a truncated hopping element $t(r)$, setting it to zero beyond a cutoff distance of $r_{\mathrm{cut}} = 3.1 d_{\mathrm{HS}}$. In the present work, the same cutoff will be applied in some calculations but a comparison to the results in the absence of the truncation will be shown. We shall present the results of calculations for our preferred value of the hopping decay $\alpha^* = 2$; for this case, $t(r_{\mathrm{cut}})/t_0 = 0.015$, which appears to be a small enough value so the thermodynamic properties should be unaffected by applying that cutoff.

Despite the simplicity of the model, exact calculations of $F_{\mathrm{el}}$ must pay a high computational price, since an $N \times N$ matrix must be diagonalized for each ionic configuration. To avoid that price, in our previous work, we developed an elaborate glue-model approximation. It consisted of basing the Monte Carlo simulations, used to obtain thermal equilibrium ionic configurations, on a self-consistent parametrization of a functional describing $F_{\mathrm{el}}$. Thus, this free energy did not need to be recalculated for each trial change in an ionic position. On each isotherm, the electronic free energy, $F_{\mathrm{el}}$ for a system with $N$ atoms at positions $\mathbf{r}_k$, was then approximated by the glue energy:

$$U_{\mathrm{glue}}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{k=1}^{N} u[\rho_1(\mathbf{r}_k), \rho_2(\mathbf{r}_k), \rho_v(\mathbf{r}_k)]. \tag{4}$$

The energy for each ion was parametrized, as a functional of its local environment, via

$$\begin{aligned} u[\rho_1, \rho_2, \rho_v] = {} & A_0 + A_1\rho_1 + A_2\rho_1\Phi + A_3\rho_1\Phi^2 + A_4\rho_1^2\Phi + A_5\rho_1\Xi \\ & + A_6\rho_1^2\Xi + A_7\rho_1\Psi + A_8\rho_1^2\Psi + A_9\rho_1\Psi^2 \\ & + A_{10}\rho_1\Psi^3. \end{aligned} \tag{5}$$

In principle, $A_0, \ldots, A_9, A_{10}$ are free, fitting, coefficients and the auxiliary functions $\Phi = 1 - \rho_2/\rho_1^2$, $\Xi = 1 - \rho_v/\rho_1^2$, and $\Psi = \Phi - \Xi$ describe the local environment of each atom, through the measures

$$\rho_1(\mathbf{r}) = \sum_{i=1}^{N} w_1(|\mathbf{r} - \mathbf{r}_i|), \quad \rho_2(\mathbf{r}) = \sum_{i=1}^{N} w_2(|\mathbf{r} - \mathbf{r}_i|),$$

$$\rho_v(\mathbf{r}) = \left| \sum_{i=1}^{N} w_2(|\mathbf{r} - \mathbf{r}_i|) \frac{\mathbf{r} - \mathbf{r}_i}{|\mathbf{r} - \mathbf{r}_i|} \right|. \tag{6}$$

The weight functions are given by

$$w_1(r) = e^{-\alpha(r - d_{\mathrm{HS}})} \text{ and } w_2(r) = e^{-2\alpha(r - d_{\mathrm{HS}})}, \tag{7}$$

for $d_{\mathrm{HS}} \leqslant r \leqslant r_{\mathrm{cut}}$ and are zero otherwise. Clearly this approach results in an enormous reduction of the computational effort. The bases of the parametrization were the exact energies of 900 configurations, arising from the model itself, of 256 particles, at each temperature and a spectrum of densities. Complete details are given in Ref. 1.

In the present work, we use exact calculations of $F_{\mathrm{el}}$, for all configurations, with a double purpose: to obtain the exact results for the thermodynamic phase coexistence and related equilibrium ionic structures of this system, and to check if the glue model is able to describe these phenomena. We had previously noted that simple versions of a glue model were inadequate to describe the thermodynamic and structural properties of interest, so we were forced to develop the more sophisticated new procedure. However, in ignorance of the exact results, we could not determine if our method was merely able to correct the pathologies of simple methods or if, more generally, it was a method with sufficient precision to have predictive capabilities. It is the main purpose of this work to allow such a determination.

## III. RESULTS

### A. Phase diagrams

In the present work, we have chosen to study the tight binding (TB-) HS model parametrization which resulted in a phase coexistence resembling that of the high-temperature

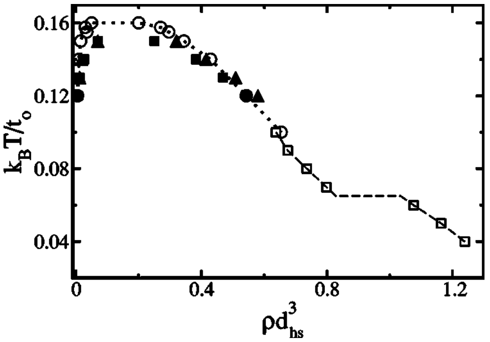

FIG. 1. Liquid-vapor phase coexistence results. At low temperature the coexistence is solid vapor. The open circles (and dotted line connecting them) are the previously published results using the glue model with a MC *NVT*-slab simulation technique and $N=1500$. The square symbols represent the present results based on the exact energy evaluations with $r_{\mathrm{cut}}=3.1d_{\mathrm{HS}}$: the open squares (and dashed line connecting them) result from the *NPT* simulations with $P=0$ and $N=256$, and the filled squares from Gibbs-ensemble simulations ($N=350$). The filled triangles represent Gibbs-ensemble simulation results ($N=350$) using the exact energies but now without truncating the electronic hopping.

region of the expanded alkali fluids, that is the one parametrized by $\alpha^*=2$.[1] Previously, we obtained the liquid-vapor coexistence curve, based on the glue-model energies and using the hopping truncation at $r_{\mathrm{cut}}=3.1d_{\mathrm{HS}}$. The simulation technique utilized an *NVT* slab; that is, a constant number of atoms ($N$) are enclosed in a volume ($V$) at a chosen temperature ($T$). The ($N=1500$) atoms were initially confined in the slab, which occupies only part of the available volume, and the MC simulation allowed evaporation into the remaining (originally empty) volume until a coexisting liquid-vapor system was equilibrated. In the present work, the liquid-vapor and, beginning at the triple point, the solid-vapor coexistence curves are obtained using the exact electronic energies. The electronic energies, at each step in the simulation, are obtained by exact diagonalizations. Since an $N\times N$ matrix diagonalization is required at each MC step, $N$ has to be kept reasonably small, but it still has to be sufficiently large to obtain reasonable thermodynamic properties. Due to the comparatively small $N$ used, the *NVT*-slab method is not appropriate. Therefore, we have performed two alternative types of simulations. To find the solid-vapor and the liquid-vapor phase diagrams at low temperatures, Monte Carlo *NPT* simulations at zero pressure have been carried out,[7] with $N=256$ particles, a reasonable approximation for a liquid (or solid) coexisting with an extremely dilute vapor phase.[8] As input configuration for these *NPT* simulations, we used the structures that minimize the energy at $T=0$. For the solid, we only tried fcc and bcc structures and the resulting equilibrium structure is fcc. With increasing vapor density, the zero pressure simulation method is not appropriate for obtaining the liquid-vapor coexistence curve at higher temperatures, so Monte Carlo Gibbs-ensemble simulations[7] have been used with a total of $N=350$ particles in the two (coexistence) boxes. Both methods incorporate periodic boundary conditions and the coexistence densities are obtained as an average over $5\times 10^5$ MC steps.

Figure 1 presents a comparison of the approximate vapor-liquid coexistence densities obtained, as a function of temperature. The present results are exhibited, from the two simulation methods based on the exact energies: *NPT* ($P=0$) and Gibbs-ensemble, and they are compared to those resulting from using the glue-model approximation of previous work and the *NVT*-slab technique. Also, a comparison is shown between results based on the exact diagonalizations but arising from cutting off the range of the hopping and those obtained dispensing with such a cutoff.

The results shown in Fig. 1 demonstrate that the phase diagram obtained with the exact energies is almost independent on whether we used $r_{\mathrm{cut}}=3.1d_{\mathrm{HS}}$ (filled squares) or dispensed with the cutoff (filled triangles). There does seem to be a general, slight, increase in the coexistence liquid densities when there is no cutoff, as expected by the increase in cohesion, but the effect is small enough to be within the margins of error due to limited statistical sampling. The insensitivity to the cutoff was expected, as noted when the truncation was justified in our previous glue-TB-HS work,[1] and is reassuring.

Figure 1 also demonstrates that our glue model does have the predictive capacity to describe the phase diagram, although there are noticeable discrepancies quite near our estimated critical point, since the results of using that glue-model approximation (open circles) are in reasonably good agreement with those from the exact energies (squares and triangles). Naturally, we can only estimate the critical conditions due to the small size of our simulation system. It should be emphasized that in order that a glue model be able to give such a good description of the phase diagram, it needs to be obtained, as ours was, guaranteeing that it reflects typical, not arbitrary, system configurations of interest. Therefore, the present results confirm the characteristics of the liquid-vapor phase diagram obtained with the glue-TB-HS. First, a very asymmetric liquid-vapor coexistence curve shape, due to many-body ionic effects which, in turn, are due to the electronic delocalization energy. Also, on comparing our results with the shape of the experimental coexistence curve of cesium,[1] the liquid branch is very similar to the results obtained here but there are clear differences for the vapor branch since our vapor densities are too low. The main difference between our results and those of real cesium vapor, at coexistence, arises from the fact that our model has a stronger tendency to produce clustering than the real material.

The estimate for the triple point temperature, obtained by using *NPT* $P=0$ simulations, is $T_t^*=0.06$; it is very similar to the value ($T_t^*=0.05$) in our previous work, arising from a perturbative approximation in which the electronically induced correlations of the ionic positions were ignored (a reasonable starting point at high ionic densities). We obtain a ratio between our estimates for the critical and the triple point temperatures of $T_c/T_t\approx 2.8$ which is to be compared with $T_c/T_t\approx 6.4$ for the alkalis, and $T_c/T_t\approx 1.8$ for the noble gases. Thus, the TB-HS model qualitatively describes the

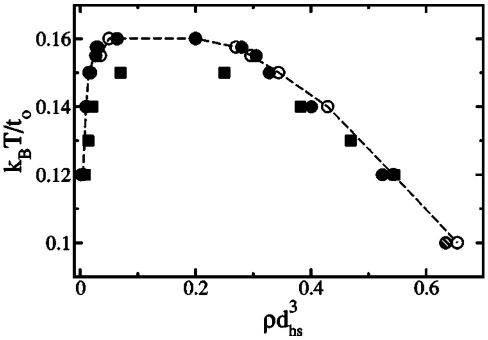

FIG. 2. Phase coexistence from *NPT* $P=0$ ($N=256$) and Gibbs-ensemble ($N=350$) simulations compared to each other and to previous work (results also shown). Open circles (and dashed line connecting them) are the previously published results using *NVT*-slab simulations ($N=1500$). Semifilled circle (at the lowest temperature) *NPT* $P=0$, $N=256$ simulation. Filled circles are results from the Gibbs-ensemble ($N=350$) simulations. All the above results are based on the same glue-model energies. The filled squares (as in Fig. 1) are results from the Gibbs-ensemble simulations based on the exact energies but without truncating electronic hopping.

tendency of the alkalis towards low melting temperatures.

It is unclear whether the differences, near our estimated critical point, between results obtained with the exact energies and those from the glue model are intrinsic, or due to a difference in simulation technique, or even to the different numbers of particles in the simulations. We have tested the effects of simulation technique and number of particles by repeating the *NPT* ($P=0$) and Gibbs-ensemble simulations, under the same conditions used in the exact calculations, but this time using the same glue-derived energies as in the previous work rather than the exact energies. The results are shown in Fig. 2. As can be seen in the figure, the results from the simulation techniques used here are in good agreement with those of our previous work, when all are based on the same glue-derived energies. Thus, the simulation techniques and the small number of particles in the exact calculations only affect the results in minor ways. The discrepancies shown in Fig. 1 are therefore due to the intrinsic differences in the configurations resulting from exact energies compared to those resulting from the glue-model energies. Although such differences are nontrivial, we judge that, for a realistic treatment of a metallic fluid, any approximation to the interaction potential (electronic screening, pseudopotential, etc.) will introduce stronger effects than those due to the glue-model treatment; hence, we consider that this type of glue-model simplification is a valid tool to study metallic fluids.

### B. Fluid structure

The results in the previous section document that calculations of the phase coexistence densities based on exact or glue-model energies are quite similar. Now we explore whether appreciable structural differences exist in the coexistence configurations obtained using the alternative methods. To make the test as rigorous as possible, we focus on conditions near our estimated critical point where the thermodynamic differences are maximized. For that purpose, new *NVT* Monte-Carlo simulations, based on the exact or glue-model energies, were carried out at densities and temperatures corresponding to the glue-derived liquid-vapor coexistence curve. In this way we can compare equilibrium configurations resulting from alternative energies at the same density and temperature. In choosing this approach there is also a guarantee that the system is stable since the liquid-vapor glue curve encloses the exact liquid-vapor curve and thus all configurations obtained in these tests are in the single phase regime. Finally, for chosen thermodynamic conditions, each set of *NVT* configurations was averaged to obtain the radial distribution function, which is also averaged over directions. Such results for $g(r)$ will be compared.

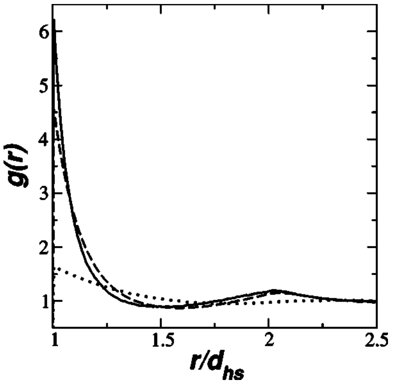

FIG. 3. Radial distribution functions $g(r)$ obtained from MC-*NVT* simulations, for a low density expanded liquid ($T^*=0.15$ and $\rho^*=0.344$). We compare the $g(r)$ arising from using exact energies with $N=256$ (solid line), that arising from using the glue-model energies with $N=500$ (dashed line), and the one obtained using the HS correlations only (dotted line).

In Fig. 3 we present three results for $g(r)$ at conditions corresponding to a low density expanded liquid: $T^*=0.15$, $\rho^*=0.344$. The results were obtained from the following simulations: those based on the exact energies ($N=256$), a change to using glue-model energies ($N=500$), and those using only HS interactions. Similarly, Fig. 4 shows the equivalent three functions but now at conditions correspond-

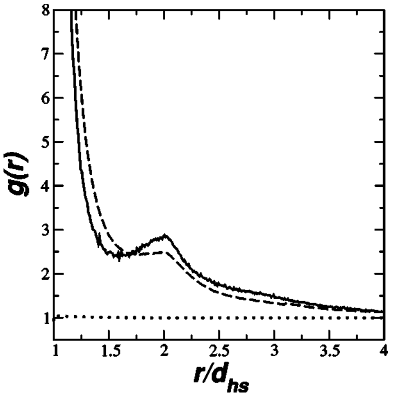

FIG. 4. Radial distribution functions $g(r)$ obtained from MC-*NVT* simulations at a high density vapor, near the transition region from metallic to nonmetallic behavior ($T^*=0.1575$ and $\rho^*=0.03$). Lines as in Fig. 3.

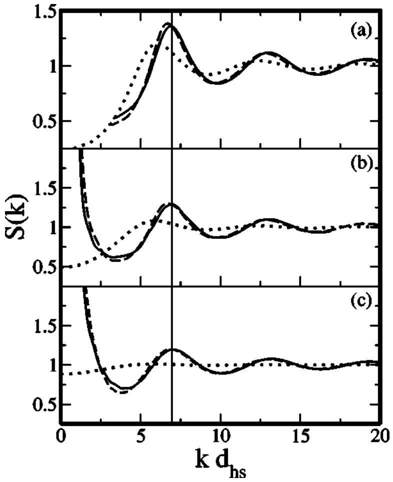

FIG. 5. Calculated static structure factors, for three points on the glue-derived liquid-vapor coexistence curve. The full lines are results from our MC-*NVT* simulations ($N=256$ particles) determined by the exact energies; the dashed lines from our MC-*NVT* simulations ($N=500$ particles) using the glue-model energies; the dotted lines are calculated assuming only HS correlations among the ions. The vertical thin line indicates the position of maxima of $S(k)$ at high density, as a reference to its position for the lower densities shown. The three densities ($T^*$ values are noted in text) correspond to (a) $\rho^*=0.344$ (a low density expanded liquid), (b) $\rho^*=0.175$ (a density very close to our estimate for the critical point), and (c) $\rho^*=0.03$ (a vapor, in the transition region from metallic to nonmetallic behavior, see Refs. 1 and 6).

ing to a high density vapor: $T^*=0.1575$, $\rho^*=0.030$. Both figures show, naturally, that the glue-model based results are closer to those based on the exact energies than those of ions correlated only by HS effects. The exact and glue results exhibit strong clustering, both in the liquid and the vapor. Also, at the liquid and the vapor densities, the radial distribution function, near the hard-sphere diameter, is substantially higher and narrower when obtained based on the exact energies than if based on the glue model. Such structural differences indicate that short-range correlations among the ionic positions, induced by the exact electronic energies, are somewhat weakened when the glue-derived energies are used. As the glue is obtained from fits to local weighted averages in configurations which themselves have different global average densities, it appears probable that the cause of part of the differences shown here might have been corrected by improved choices for the weight functions in the glue model of our previous work [Eq. (7) of the present article].

Nonetheless, as the glue-model approach has been found adequate for the thermodynamic calculations, one should not overemphasize the importance of structural differences such as those shown in Figs. 3 and 4. This point of view is reinforced on examining the static structure factors $S(k)$ along the coexistence curve; results for $S(k)$ are shown in Fig. 5. Note that the density and temperature conditions in this figure not only include those corresponding to Figs. 3 and 4 but also include a set of conditions very close to our estimate for the critical point ($T^*=0.16$, $\rho^*=0.175$). Overall, the static structure factor resulting from the glue-based simulations can be seen to show a slight shift to smaller wave number compared to that based on the exact energies, this is the same effect already observed in the radial distribution functions. However, the effect is small and the figure demonstrates that the glue model yields a reasonably faithful representation of the exact static structure factor for the three densities. Such structural fidelity justifies the good results for the thermodynamic properties.

As an aside to the main thrust of this paper, to compare the structural properties of the present model to those of the real alkali fluids, one must keep in mind two principal properties of the real systems:[9] the softness of the repulsive part of the effective potential, which causes the initial increase of $g(r)$ to become more gradual as the temperature increases, and the observation that $S(k)$, at low $k$ values, exhibits a strong increase at high temperature, even quite far from the critical point. Regarding the first property, the softness of the repulsive potential is certainly not included in our model, which assumes hard spheres. In fact, $S(k)$ in our model exhibits a strong oscillatory structure even on increasing the temperature, in contrast to the oscillation damping observed[10] for cesium and rubidium. The robustness of the oscillatory structure is a hard-sphere effect. It, in fact, corresponds to such an effect for spheres of larger diameter than that chosen in the model, a result due to the clustering induced by the electronic energy. If a soft repulsion had been chosen for the model, the oscillatory structure of $S(k)$ would have been damped as the temperature increased.[8] The second observation, however, does result from the model, as can be seen in Fig. 5. As in the real systems, our structure factor shows a strong increase at low $k$-values as the density is lowered, in the vapor phase, from the critical regime. Though a compressibility divergence at the critical point is well known, the phenomenon under discussion is distinct and this effect, in the model, is even more pronounced than that in the real systems. Such an enhancement reflects the presence of dimers, trimers, and larger clusters, which form a higher fraction of our model system than in the real alkali fluids. A low-$k$ enhancement in the structure factor reflects a compressibility increase, which will clearly result from an increase in clustering since the free volume is then enhanced. The low-$k$ enhancement in $S(k)$ results from both the calculations based on the exact energies and, as previously noted, the glue-model based ones; thus, the model reflects the experimentally observed effect. Calculations for expanded rubidium,[11] within the optimized random-phase approximation, give evidence that this enhancement is due to a breakdown of the nearly free-electron approximation in a regime where the mean free path of the electrons becomes smaller than the average interatomic distance. Obviously such an effect is being included in our model and is associated with the formation of clusters; however, if there were no such strong clustering the enhancement would be somewhat muted.

### C. Electronic properties

In this section, we discuss the influence of clustering and inhomogeneities in structure, arising from the electronically

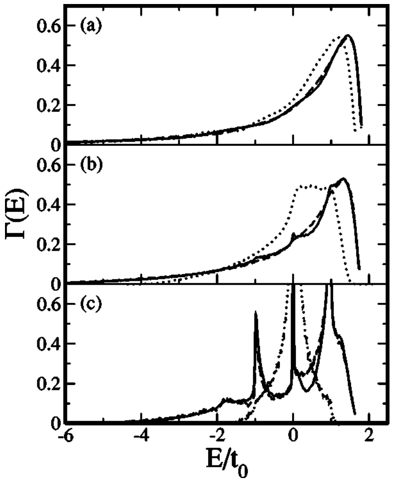

FIG. 6. Electronic density of states per ion $\Gamma(E)$ as function of $E/t_o$ for the same three sets of conditions as in Fig. 5. The full lines give the results obtained using ionic configurations from our MC-*NVT* simulations ($N=256$ particles) based on the exact energies; the dashed lines from our MC-*NVT* simulations ($N=500$ particles) using the glue-model energies; the dotted lines are calculated assuming only HS correlations among the ions.

induced positional correlations among ions, on the electronic density of states. We compare the results obtained from the exact and glue-derived configurations. In Fig. 6 we present the electronic density of states per ion $\Gamma(E)=\langle\Sigma_k\delta(E-\epsilon_k)\rangle/N$; we again make the test rigorous by choosing the same three sets of thermodynamic conditions as were chosen for Fig. 5. The results have been obtained using *NVT* Monte Carlo simulations, 2000 configurations were averaged with a configuration being chosen after each 100 MC steps. For comparison, we include, in the same figure, the $\Gamma(E)$ calculated based on MC runs evolving with exact energy (full line), with the glue energy (dashed line),[12] and exclusively with HS interactions. The main conclusion drawn from the comparison of the electronic density of states is that, also in examining this property, there is no indication of qualitatively different structural effects arising from basing the simulations on the exact rather than the glue-derived energies, for the three sets of conditions. Therefore, we conclude that the glue model is sufficiently accurate in describing ionic configurations, in the entire density range considered, so that there is negligible difference between the electronic density of states derived from such configurations and that resulting from an exact evaluation of the system energies. Gross structural differences are certainly observable, as is evident in the comparisons with the case in which there are only HS correlations; more subtle structural differences are also detectable in the electron density of states.[12] Comparison of conductivity results for the model,[6] arising from the exact and glue approaches, certainly probes more details than merely the density of states but also yields good agreement. Thus, a negligible difference is expected on calculating any electronic property of realistic models for metallic fluids, whether the calculation be based on configurations derived from exact energies or from this type of glue model.

Once again we conclude, based on the present exact energy calculations as was the case based on the previous glue-model results, that it is only reasonable to describe the system as one with HS correlations for dense liquids ($\rho^* \geqslant 0.35$), in order to obtain realistic electronic densities of states. The difference between $\Gamma(E)$ obtained with the exact or glue correlations and the one based on HS correlations becomes increasingly larger as the density decreases, the difference is quite large on reaching the vapor side of the coexistence curve. In such density regimes, the glue and the exact calculations result in a $\Gamma(E)$ which remains quite similar to that in the dense liquid but stronger peak structures, due to localized electronic states, begin to appear, first localized on atoms, at $\rho^*=0.175$, and then on atoms, dimers, and trimers, at $\rho^*=0.03$. In contrast, assuming HS correlations at such a low bulk densities leads to an electronic density of states with a strong, narrow, and symmetric band near the energy corresponding to isolated atoms. More details are given in Ref. 1.

### D. Final remarks

Our first conclusion, based on using the exact energies of this work for the MC simulations, is that the thermodynamic properties of the TB-HS model can be adequately obtained, as was done in Ref. 1, using a suitable glue-type fitting to describe the energies of atoms as a function of their environment. This conclusion is important, as using glue-derived energies is one of the few ways that calculations for this type of metallic fluid problem can be simplified for computational efficiency. It is worth emphasizing this conclusion, as we had already shown that perturbative mean-field methods are not at all appropriate to the present problem. The present work also confirms the results for the TB-HS model obtained previously with the glue-model treatment: an asymmetric vapor-liquid coexistence curve which is similar to that observed experimentally for the alkali fluids, the electronically induced correlations are more important in this model than in real alkali fluids, and the electronic density of states at low densities depends dramatically on the self-consistency between the ionic and the electronic structures.

Generalizing, suppose that instead of considering the present, somewhat artificial, TB-HS model for a hot metallic fluid one considered using a realistic model, with pseudopotentials describing the electron-ion interaction, taking into account screening, electron-electron interactions, and some soft-sphere ion-ion interaction, in order to calculate the thermodynamic, structural, and electronic properties of the fluid. Our results suggest that using a few hundred atoms and allowing a self-consistent electron-ion treatment can form the basis for a suitable glue-model fitting of the atom energies as a function of local environments, with a computational burden which, though heavy, is comparable or lighter than that undertaken in this work. The burden would certainly be heavier that that shouldered to obtain our glue-model fits. Attempting to continue, without the glue parametrization, for the millions of MC steps required for an adequate statistical sampling of the thermodynamic properties would be prohibitive. Yet, with the glue-model fits, studying an adequate spectrum of configurations for the statistical sampling seems indeed feasible. Our comparison of properties based on a glue model and those obtained from using exact energies for the TB-HS model suggests that the above procedure, for a realistic treatment, would yield accurate results. We suggest that this is the most important conclusion to be drawn from our effort.

---

[1] M. Reinaldo-Falagán, P. Tarazona, E. Chacón, E. Velasco, and J. P. Hernandez, Phys. Rev. B **67**, 024209 (2003).

[2] M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).

[3] K. W. Jacobsen, J. K. Norskov, and M-J. Puska, Phys. Rev. B **35**, 7423 (1987).

[4] M. W. Finnis and J. E. Sinclair, Philos. Mag. A **50**, 45 (1984); W. Zhong, Y. S. Li, and D. Tomanek, Phys. Rev. B **44**, 13 053 (1991); M. M. Sigalas, and D. A. Papaconstantopoulos, *ibid.* **49**, 1574 (1994)

[5] F. Ercolessi, E. Tosatti, M. Parrinello, Phys. Rev. Lett. **57**, 719 (1986); F. Ercolessi, M. Parrinello, and E. Tosatti, Philos. Mag. A **58**, 213 (1988).

[6] P. Tarazona, E. Chacón, J. A. Vergés, M. Reinaldo-Falagán, E. Velasco, and J. P. Hernandez, Phys. Rev. B **71**, 024203 (2004), the preceding paper.

[7] D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic, New York, 1996).

[8] E. Velasco, P. Tarazona, M. Reinaldo-Falagán, and E. Chacón, J. Chem. Phys. **117**, 10 777 (2002)

[9] F. Hensel and W. W. Warren Jr., *Fluid Metals* (Princeton University Press, Princeton, 1999).

[10] R. Winter, T. Bodensteiner, W. Gläser, and F. Hensel, Ber. Bunsenges. Phys. Chem. **91**, 1327 (1987); R. Winter, F. Hensel, T. Bodensteiner, and W. Gläser, J. Phys. Chem. **92**, 7171 (1988)

[11] G. Kahl and J. Hafner, Phys. Rev. A **29**, 3310 (1984)

[12] It should be noted that the results in Fig. 6, for $\rho^* = 0.175$ and labeled as derived from the glue-model treatment, are different from similarly labeled ones in Ref. 1. The difference is due to the fact that the previously published results, at these conditions, were based on configurations with insufficient averaging so that the formation of a vapor bubble, which took place, fictitiously increased the contributions from essentially isolated atoms and dimers to the electronic density of states. The results in the present figure are correctly averaged.