New Molecular-Dynamics Method for Metallic Systems

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We present a new formulation for simulations of metallic systems which allows for volume and shape variations and incorporates explicitly the dependence on density of the "volume energy" and the effective pair potentials. Simulations of liquid Mg yield good agreement with experiments for several properties including internal energy, density, and structure factors at several temperatures (T) and pressures (P). Correlations between fluctuations in T, P, and volume are in approximate agreement with the appropriate thermodynamic relations.

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Molecular-dynamics (MD) simulations, which consist of the numerical solution of the equations of motion of a many-particle system, have become an important theoretical tool in investigations of the microscopic structure and dynamics of material systems. Practical simulations of extended systems involve up to a few thousand particles (N), contained in a calculational cell (CC) which is repeated via periodic boundary conditions.[1] In earlier work the volume (Ω) of the CC was kept constant, thus yielding phase-space trajectories of an (N,Ω,U) ensemble (or a microcanonical ensemble since the internal energy U is conserved). To study phenomena which inherently involve changes in volume or structure several new methods have been proposed and implemented, such as the *Ansatz* Lagrangian[2,3] and constrained-dynamics[1] techniques.

Underlying the structural and dynamical properties are the various contributions to the total energy of the material. While for the rare-gas, molecular, and ionic systems a satisfactory description may be given in terms of pairwise (and higher-order) interactions, it is well known that the cohesive energy of a metal contains, in addition, density-dependent contributions which are structure independent and that the metallic effective pair potentials themselves depend on conduction-electron density.[4]

In the new method which we have developed the volume-dependent contributions to the energy are explicitly included in the derivation of the Lagrangian equations of motion. The method thus circumvents the need to impose artifically an external "electron pressure" in the simulation and is designed for studies of equilibrium and nonequilibrium phenomena involving volume and structural changes in metallic systems.

Consider a metallic alloy with N_σ particles of species σ and a total number of particles $N=\sum_\sigma N_\sigma$ contained in a CC of volume Ω. The periodic replications of the CC are labeled by $\mathbf{l}=(l_1,l_2,l_3)^T$ with $l_\alpha=0,\pm1,\pm2,\ldots$ $(\alpha=1,2,3)$, and the position of particle j in cell $\mathbf{l}$ is given by $\mathbf{r}_j(\mathbf{l})=\mathbf{H}\cdot(\mathbf{s}_j+\mathbf{l})$, where $\mathbf{s}_j=(s_{j1},s_{j2},s_{j3})^T$, $-\frac{1}{2}<s_{j\alpha}<\frac{1}{2}$ $(\alpha=1,2,3)$, and $\mathbf{H}$ is a 3×3 matrix with $\det(\mathbf{H})=\Omega$. The cohesive energy for a simple metal alloy can be written as[4]

$$E_T=E_\Omega+\tfrac{1}{2}{\sum_{i,j,\mathbf{l}}}'\phi_{ij}^{(2)}(r_s,r_{ij}(\mathbf{l})), \tag{1a}$$

$$E_\Omega=\sum_\sigma N_\sigma[Z_\sigma E_{\rm el}(r_s)+\phi_\sigma^{(1)}(r_s)], \tag{1b}$$

where $r_{ij}(\mathbf{l})\equiv|\mathbf{r}_i-\mathbf{r}_j(\mathbf{l})|$, r_s is the electron density parameter, Z_σ is the valence number, $E_{\rm el}$ is the energy of the uniform electron gas, and $\phi_\sigma^{(1)}$ is a single-particle contribution. $\phi^{(1)}$ and the density-dependent effective pair potential $\phi^{(2)}$ are derived via pseudopotential theory[4] and their specific form depends upon the choice of ionic pseudopotentials (model, local, nonlocal).

To allow for temporal volume and shape variations the components of the matrix $\mathbf{H}$ are taken as dynamical variables. The *Ansatz* Lagrangian is obtained by replacement of all the terms in the kinetic energy which involve $\dot{\mathbf{H}}$ with $\frac{1}{2}W\,\mathrm{Tr}(\dot{\mathbf{H}}^T\cdot\dot{\mathbf{H}})$, where W has the dimension of mass, yielding

$$\mathscr{L}=\tfrac{1}{2}\sum_i m_i\dot{\mathbf{s}}_i^T\cdot\mathbf{G}\cdot\dot{\mathbf{s}}_i-\tfrac{1}{2}{\sum_{i,j,\mathbf{l}}}'\phi_{ij}^{(2)}(r_s,r_{ij}(\mathbf{l}))+\tfrac{1}{2}W\,\mathrm{Tr}(\dot{\mathbf{H}}^T\cdot\dot{\mathbf{H}})-E_\Omega(r_s)-P_{\rm ext}\Omega, \tag{2}$$

where $\mathbf{G}=\mathbf{H}^T\cdot\mathbf{H}$. The above Lagrangian extends that of Parrinello and Rahman[2] to include the volume energy $E_\Omega(r_s)$ and the volume dependence in the pair potentials. The restriction to volume variation only (Andersen's Lagrangian[3]) is obtained by setting $\mathbf{H}=L\hat{\mathbf{H}}$, where $\hat{\mathbf{H}}$ is a constant matrix and L is a dynamical variable with the dimension of length. With the definitions $V_{ij}(r_s,X_{ij}(\mathbf{l}))=\phi_{ij}^{(2)}(r_s,r_{ij}(\mathbf{l}))$, where $X_{ij}(\mathbf{l})=r_{ij}(\mathbf{l})/r_s$, and $\chi_{ij}(r_s,X)=-(1/X)\partial V_{ij}(r_s,X)/\partial X$, and with the prime denoting derivatives with respect to r_s, the Lagrangian

equations of motion follow:

$$m_i\ddot{\mathbf{s}}_i = r_s^{-2}\sum_{j,1}{}'\chi_{ij}(r_s,X_{ij}(1))\mathbf{s}_{ij}(1) - \mathbf{G}^{-1}\cdot\dot{\mathbf{G}}\cdot\dot{\mathbf{s}}_i, \tag{3a}$$

$$W\ddot{\mathbf{H}} = \mathbf{H}\cdot\sum_i m_i\dot{\mathbf{s}}_i\dot{\mathbf{s}}_i^{T} + \tfrac{1}{2}r_s^{-2}\mathbf{H}\cdot\sum_{i,j,1}{}'\chi_{ij}(r_s,X_{ij}(1))\mathbf{s}_{ij}(1)\mathbf{s}_{ij}(1)^{T}$$

$$-(\mathbf{H}^{-1})^{T}\left(\frac{1}{6}\sum_{i,j,1}{}'[r_s V_{ij}'(r_s,X_{ij}(1)) + X_{ij}(1)^2\chi_{ij}(r_s,X_{ij}(1))] + P_{\text{ext}}\Omega + \tfrac{1}{3}r_s E_{\Omega}'(r_s)\right). \tag{3b}$$

For a constant-shape MD CC, Eq. (3b) is replaced by

$$W\,\mathrm{Tr}(\mathbf{G})L^{-1}\ddot{L} = \sum_i m_i\dot{\mathbf{s}}_i^{T}\cdot\mathbf{G}\cdot\mathbf{s}_i - r_s\left(\frac{1}{2}\sum_{i,j,1}V_{ij}'(r_s,X_{ij}(1)) + E_{\Omega}'(r_s)\right) - 3\Omega P_{\text{ext}}. \tag{3c}$$

For calculations of dynamical properties a proper magnitude of the mass parameter W is to be chosen. Adopting the approach of Andersen[3] we start from an approximate equation of motion for the cell volume Ω, $d^2\Omega^{1/3}/dt^2 = W^{-1}(P - P_{\text{ext}})\Omega^{2/3}$, where the internal pressure is given by $P \simeq -3B_s(1 - \Omega^{1/3}/\langle\Omega\rangle^{1/3})$ and B_s is the adiabatic bulk modulus. The wavelength of the acoustic phonon, whose frequency equals that of the volume oscillations determined from the above equation $[\omega_{\Omega} = (3B_s\Omega^{1/3}/W)^{1/2}]$, is $\lambda_{\Omega} = 2\pi(W/3M)^{1/2}\Omega^{1/3}$, where M is the total mass of the particles in the CC. Modes with $\lambda \leq L$, where L approximates the linear dimension of the CC, are already present in the simulation; we choose W such that $\lambda_{\Omega} \simeq 2.5L$.

To illustrate the method we carried out simulations of liquid magnesium at several temperatures and external pressures. Since liquids do not resist shear stresses, random fluctuations in the CC shape may eventually result in undesirable cell shapes which lead to interactions between particle images. To alleviate this problem and to minimize any deviation in spherical symmetry due to the periodic boundary conditions, we have used Eq. (3c) (constant-shape CC) with $\hat{\mathbf{H}}$ chosen so that $\hat{\mathbf{H}}\cdot\mathbf{1}$ describes an fcc lattice. The single-particle and pair-particle potentials, $\phi^{(1)}$ and $\phi^{(2)}$, were obtained from a simplified Heine-Abarenkov ionic pseudopotential[5] with exchange correlation included via the Singwi *et al.*[6] local-field correction. In addition, the Hartree contribution to $\phi^{(1)}$ was scaled by a parameter z_{H}.[7] The pseudopoential parameters r_c, u_c, and z_{H} were chosen to fit exactly the zero-temperature cohesive energy, bulk modulus, and density and to give the correct, hcp, crystalline structure ($r_c = 1.824a_0$, $u_c = 0.5484$ Ry, $z_{\text{H}} = 0.9407$). The resulting pair potential and its derivative with respect to r_s are shown in Fig. 1, for densities corresponding to 0 K and that of the liquid at 960 K. The integration time step was $\Delta t = 1.46\times10^{-15}$ sec and $N = 500$ particles. Simulations were performed for $P_{\text{ext}} = 0$ at three temperatures, 960, 1070, and 1150 K, and for $P_{\text{ext}} = 0.1$ mRy/a_0^3 at $T = 1070$ K [T(melting) = 922 K]. The period of volume oscillations was found to be $t_{\Omega} \simeq 1300\Delta t$. The results shown in Table I are averaged over intervals of at least $5t_{\Omega}$ for the equilibrated samples, chosen so that the average particle and cell temperatures [left- and right-hand sides in Eq. (4), respectively] were approximately equal:

$$(3N-3)^{-1}\langle\textstyle\sum_i m_i\dot{\mathbf{s}}_i^{T}\cdot\mathbf{G}\cdot\dot{\mathbf{s}}_i\rangle \simeq \langle W\,\mathrm{Tr}(\dot{\mathbf{H}}^{T}\cdot\dot{\mathbf{H}})\rangle. \tag{4}$$

As mentioned above, an advantage of the present formulation is that the internal pressure P of the system [Eq. (5)] contains all contributions and at equilibrium, $\langle P\rangle = P_{\text{ext}}$, which yields the correct density. The internal (virial) pressure is given by

$$P = \left(-r_s\left[E_{\Omega}'(r_s) + \tfrac{1}{2}\sum_{i,j,1}{}'V_{ij}'(r_s,X_{ij}(1))\right] - \sum_i m_i\dot{\mathbf{s}}_i^{T}\cdot\mathbf{G}\cdot\dot{\mathbf{s}}_i\right)(3\Omega)^{-1}. \tag{5}$$

At $T = 960$ K, the volume, pair-potential, and kinetic contributions to $\langle P\rangle$ are -0.55, 0.52, and 0.03 mRy/a_0^3, respectively.

We have calculated, in addition to average thermodynamic quantities, their mean square deviations for which the following relations hold in the isoenthalpic-isobaric ensemble[12]:

$$c_p = \left[\frac{2}{3} - \frac{N\langle\Delta T^2\rangle}{\langle T\rangle^2}\right]^{-1}, \qquad B_s = \frac{\langle\Omega\rangle\langle T\rangle}{\langle\Delta\Omega^2\rangle},$$

where c_p is the isobaric specific heat per atom; B_s is the adiabatic bulk modulus; T, the kinetic temperature, is defined as twice the instantaneous kinetic energy per degree of freedom; and angular brackets indicate a time average.

The results obtained are shown in Table I along with available experimental values. The internal energy, U, is the sum of the potential- and kinetic-energy terms in the Lagrangian, but with omission of the term in-

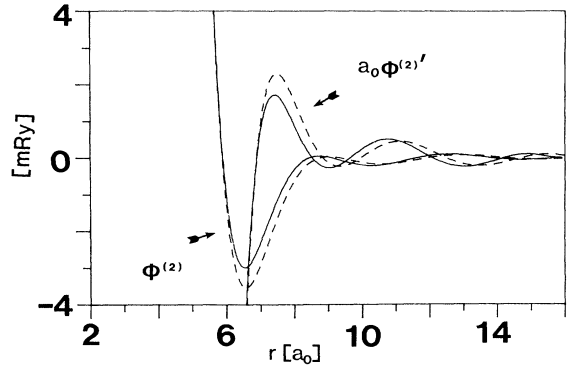

FIG. 1. Effective pair potential, $\phi^{(2)}$, and derivative with respect to r_s, $\phi^{(2)\prime}=\partial\phi^{(2)}/\partial r_s$, plotted vs interparticle distance, r, for densities corresponding to temperatures of 0 K ($r_s=2.650a_0$, solid lines) and 960 K ($r_s=2.764a_0$, dashed lines).

volving $\dot{\mathbf{H}}$. The experimental values for U are obtained from the cohesive energy at $T=0$,[8] the ionization energy,[9] the heat of melting,[8] and $c_p(T)$ for liquid and crystalline phases.[10] The thermal expansion coefficient, $\alpha=r_s^{-1}\partial r_s/\partial T$, is obtained from a two-parameter fit to the simulation results, $r_s=a_0(5.404\times10^{-2}-6.94\times10^{-6}T\,[\mathrm{K}])^{-1/3}$. The agreement between experiment and simulation for U, r_s, and α is quite good considering the uncertainty in the experimental values and the fact that a simple local model pseudopotential fit to $T=0$ properties was used in the simulation. The experimental value of B_T was obtained from that of B_s, and the measured value[11] of $B_T/B_s=0.75$ (at melting). The entries in Table I labeled "(diff)" were estimated from differences in $U(T,P)$. Reliable experimental values for c_p are available only near melting, and c_p is estimated[10] to be constant over the temperature range of our simulations, while our results indicate that c_p decreases with increasing T. The differences between the experimental and estimated (diff) quantities and the corresponding thermodynamic relations involving fluctuations may be attributed to the small number of particles ($N=500$) and the difficulty in adequately sampling the phase space due to the time scale associated with volume oscillations [see discussions preceding Eq. (4)]. Finally, we have calculated the diffusion constants, D, via the velocity autocorrelation functions, and the electrical resistivity, ρ, and thermopower, Q, using the Faber-Ziman theory[13] and the static structure factors obtained from the simulation (the correspond-

TABLE I. Simulation results and comparison with available experimental data (expt). Angular brackets indicate time averages (see text). With the exception of B_T(diff), all simulation results correspond to $\langle P\rangle=P_{\mathrm{ext}}=0$.

$\langle T\rangle$	960 K	1070 K	1150 K
U/N (expt) (Ry)[a]	−1.762	−1.759	−1.757
$\langle U/N\rangle$	−1.7496	−1.7464	−1.7443
r_s(expt) (a_0)[b]	2.741	2.759	2.772
$\langle r_s\rangle$	2.764	2.779	2.790
α(expt) (10^{-5} K^{-1})[b]	5.63	5.73	5.83
α	4.88	4.97	5.03
c_p/k_B (expt)[c]	3.9	3.9	3.9
c_p(diff)/k_B[d]	4.88	4.27	3.90
$[\frac{2}{3}-(\langle T\rangle^2/N\langle\Delta T^2\rangle)^{-1}]^{-1}$	3.8	4.7	3.8
B_s(expt) (mRy/a_0^3)[e]	1.75	1.67	1.60
$\langle\Omega\rangle\langle k_BT\rangle/\langle\Delta\Omega^2\rangle$	1.76	1.68	1.70
$\omega_\Omega^2 W/3\langle\Omega^{1/3}\rangle$	1.4	1.3	1.3
B_T(expt)[e]	1.31	1.25	1.20
B_T(diff)[d]		1.4	
D (10^{-5} cm^2/sec)	2.4	3.6	4.9
ρ ($\mu\Omega$ cm)	16.5	16.0	15.8
Q (μV/K)	1.45	2.47	2.82

[a]References 8, 9, and 10.
[b]Reference 9.
[c]Reference 10.
[d]Estimated from differences (see text); the averages of the two temperatures used to obtain c_p(diff) are 1015, 1055, and 1100 K, respectively.
[e]Reference 11.

ing pair-correlation function at $T=960$ K is in good agreement with experiment[14]). Our results of a positive Q and negative $d\rho/dT$ are typical of divalent liquid metals. Experimental values for ρ and Q at melting are 27 $\mu\Omega$ cm and 1.5 μV/k, respectively.[15]

In conclusion, we have developed an *Ansatz* Lagrangian method for the MD simulation of simple metal systems in which the density dependence of both the structure-dependent "volume-energy," E_Ω, and the effective pair potential is explicitly included. The volume (and optionally the shape) of the MD CC is a dynamic variable; the cell responds to pressure fluctuations and there is no need to impose an external "electronic" pressure to achieve the correct density. The method is thus suited to simulation of processes which involve changes in temperature, pressure, and/or volume such as crystal nucleation and the formation and annealing of a metallic glass. Since fluctuations in these quantities are predicted to play an important role in the nonequilibrium processes mentioned above,[16] our method should result in a more realistic simulation of such processes than the conventional constant-volume or density-independent potential simulations.

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