

# Generating inherent structures of liquids: Comparison of local minimization algorithms

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Potential-energy landscape (PEL) analysis plays an important role in understanding the behavior of a number of complex many-body systems, including liquids and glasses.<sup>1-3</sup> An important feature of the PEL is the presence of inherent structures, which are defined as the local minima of the configurational potential energy  $U(\mathbf{x})$ , where  $\mathbf{x}$  is the  $3N$ -dimensional position vector of the  $N$ -body system. To locate the significant inherent structures of a system in a particular thermodynamic state, instantaneous configurations are sampled from an appropriate Monte Carlo or molecular-dynamics simulation trajectory. Steepest descent (SD) mappings from each instantaneous configuration are then used to generate an ensemble of inherent structures. A steepest descent mapping is rigorously defined by the first-order differential equation:

$$\frac{d\mathbf{x}}{ds} = -\nabla U(\mathbf{x}), \quad (1)$$

where  $s$  is a scalar progress variable. A standard numerical implementation of such a minimization procedure typically involves successive iterations, where each iteration corresponds to moving from a current point  $\mathbf{x}$  to a point  $\mathbf{x}'$ , where  $\mathbf{x}'$  is obtained by finding the minimum in the direction  $-\nabla U(\mathbf{x})$ . The procedure may be slow because of nonorthogonality of successive search directions, especially if the ratio of largest to smallest eigenvalues of the Hessian at the minimum is large, as is typically of the case in molecular solids and liquids. As a consequence, PEL studies usually employ gradient-based local minimization methods that are more efficient than the SD algorithm.<sup>4</sup> It is generally assumed that the average properties of an ensemble of inherent structures obtained by any standard gradient-based minimization algorithm will not differ significantly from those of the true steepest descent minima, though we are not aware of explicit tests in the literature.<sup>3</sup> Given the importance of inherent

TABLE I. Comparison of the average properties of local or quenched minima obtained by conjugate gradient (CG) and limited-memory Broyden-Fletcher-Goldfarb-Shanno (LBFGS) algorithms.  $N_c$  configurations were sampled from  $NPT$  ensemble simulations at a reduced pressure,  $P=0.67$ ; the temperatures  $T$  and mean reduced densities  $\rho$  are shown. Energies and return distances are reported in reduced units of the pair binding energy  $\epsilon$  and the LJ length parameter  $\sigma$ . The CG quenches were assumed to be converged when the change in energy between two successive iterations was less than  $10^{-8}\epsilon$ , which typically corresponded to a rms gradient value of  $0.003\epsilon/\sigma$ . The LBFGS minimization was assumed to be converged when the rms gradient was less than  $10^{-4}\epsilon/\sigma$ .

$T$	$\rho$	$N_c$	LBFGS		CG	
			$\langle U_L \rangle$	$\langle \delta_L \rangle$	$\langle U_C \rangle$	$\langle \delta_C \rangle$
1.300	0.564	200	-1414.67 ( $\pm 1.62$ )	1.510 ( $\pm 0.009$ )	-1416.34 ( $\pm 1.69$ )	1.289 ( $\pm 0.009$ )
1.200	0.611	200	-1435.73 ( $\pm 1.55$ )	1.257 ( $\pm 0.007$ )	-1440.17 ( $\pm 1.54$ )	1.169 ( $\pm 0.007$ )
1.100	0.652	200	-1458.48 ( $\pm 1.33$ )	1.072 ( $\pm 0.006$ )	-1458.69 ( $\pm 1.36$ )	1.064 ( $\pm 0.007$ )
1.000	0.696	200	-1481.06 ( $\pm 1.16$ )	0.967 ( $\pm 0.005$ )	-1479.88 ( $\pm 1.18$ )	0.963 ( $\pm 0.006$ )
0.900	0.742	200	-1504.43 ( $\pm 1.15$ )	0.853 ( $\pm 0.005$ )	-1506.53 ( $\pm 1.25$ )	0.864 ( $\pm 0.005$ )
0.800	0.783	100	-1529.99 ( $\pm 1.46$ )	0.766 ( $\pm 0.007$ )	-1528.77 ( $\pm 1.38$ )	0.769 ( $\pm 0.006$ )
0.750	0.804	100	-1541.08 ( $\pm 1.63$ )	0.732 ( $\pm 0.007$ )	-1540.11 ( $\pm 1.49$ )	0.727 ( $\pm 0.006$ )
0.725	0.815	100	-1549.88 ( $\pm 1.51$ )	0.710 ( $\pm 0.006$ )	-1551.48 ( $\pm 1.75$ )	0.719 ( $\pm 0.006$ )
0.700	0.825	100	-1553.37 ( $\pm 1.25$ )	0.701 ( $\pm 0.006$ )	-1553.27 ( $\pm 1.58$ )	0.705 ( $\pm 0.007$ )
0.675	0.834	100	-1563.82 ( $\pm 2.22$ )	0.694 ( $\pm 0.008$ )	-1561.93 ( $\pm 1.71$ )	0.682 ( $\pm 0.006$ )
0.650	0.845	100	-1568.69 ( $\pm 1.36$ )	0.642 ( $\pm 0.008$ )	-1569.94 ( $\pm 1.55$ )	0.652 ( $\pm 0.007$ )

structure analysis in understanding liquids and complex fluids, we feel it is useful to address this computational issue. Therefore, in this note, we consider a liquid whose particles interact via a pair-additive Lennard-Jones interaction, modified to ensure continuity of derivatives of all orders.<sup>5,6</sup> We compare the properties of the minima obtained by two different local minimization algorithms: the conjugate gradient (CG) and the limited-memory Broyden-Fletcher-Goldfarb-Shanno (LBFSGS).<sup>4,7</sup>

The CG algorithm is a modified SD technique with the successive descent directions chosen to be conjugate to preceding directions and an accurate line minimization is performed along each search direction.<sup>4</sup> The LBFSGS algorithm is a quasi-Newton method where gradient information from successive iterations are used to build an approximate Hessian.<sup>7</sup> Quasi-Newton techniques compute a descent direction as well as a probable step size at the start of each iteration and therefore require less demanding line minimization algorithms than the CG method. The CG method has been more widely used in the context of inherent structure analysis than the LBFSGS algorithm, though the latter appears to be significantly more efficient.<sup>3</sup>

For a system of 256 particles interacting through the modified Lennard-Jones potential defined in Ref. 6, we perform isochoric quenches using configurations sampled from *NPT* ensemble simulations in the solid and liquid phases and compare the inherent structure configurational energies ( $U_q$ ) and return distances ( $\delta_q$ ). For a given instantaneous configuration  $\mathbf{x}$ , the return distance  $\delta_q = \sqrt{(1/N)\sum_i^N(\mathbf{x}_i - \mathbf{q}_i)^2}$ , where  $\mathbf{q}$  is the position vector of the corresponding inherent structure and the summation extends over all atoms  $i$  in the configuration. In the solid phases, both the CG and LBFSGS quenches give identical results. The results for the liquid phase are shown in Table I where we compare the average inherent structure energy  $\langle U_q \rangle$  and the return distance  $\langle \delta_q \rangle$ , with the subscript  $q$  equal to  $L$  or  $C$  corresponding to the LBFSGS or CG procedure, respectively. The average inherent structure energies obtained by the two algorithms agree within the first standard deviation for 10 of the 11 temperatures studied here. The differences between the average return distances obtained by the two procedures are somewhat larger.

Inspection of individual configurations shows that for a given starting configuration, the two minimization methods can give different values of  $U_q$  and  $\delta$ . Figure 1(a) displays the correlation between the inherent structure energies,  $U_C$  and  $U_L$ , obtained using the CG and LBFSGS techniques for the same starting configuration. There is a significant degree of scatter about the  $U_C = U_L$  line which increases with temperature. The correlation plot for the return distances shown in Fig. 1(b) is similar except that the extent of scatter is larger. It would, therefore, appear that small differences in the minimization pathway can lead to somewhat different final configurations, even though both the CG and LBFSGS

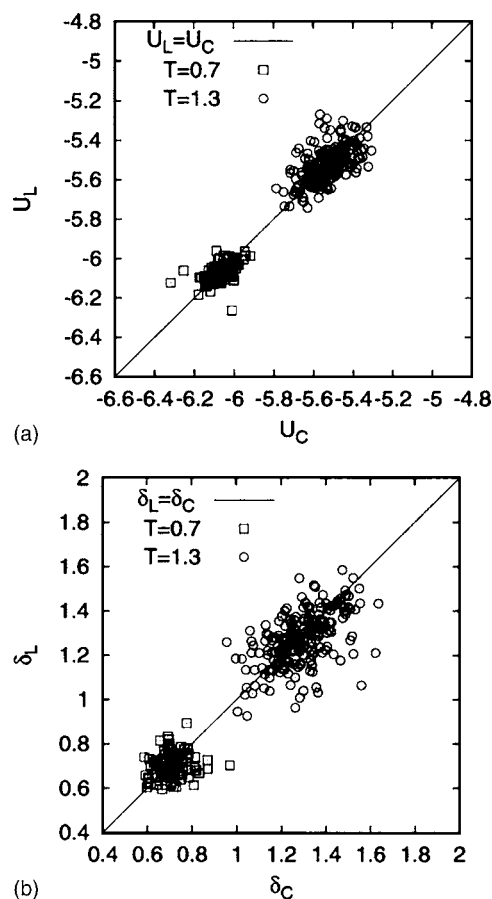


FIG. 1. Correlation plot of (a) the inherent structure energies ( $U_C$  and  $U_L$ ) and (b) return distances ( $\delta_C$  and  $\delta_L$ ) for minima obtained by CG and LBFSGS methods, respectively, for a set of 100 minima sampled from *NPT* simulations at  $T=1.3$  and  $T=0.7$  along the  $P=0.67$  isobar.

algorithms sample inherent structures with very similar properties.

We conclude that if the relevant portions of the basins of local minima are smooth, as in the solid phase, both algorithms should give identical results, but on a rough landscape with a high density of local minima, the two algorithms may not quench to identical minima, given the same starting configuration. The latter situation should be typical of liquids where the rough energy landscape must be a counterpart of the chaotic dynamics seen in the corresponding classical trajectories. If, however, statistical properties of minima are of interest, then either method will yield the same average properties.

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