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The Infinite-Volume Ground State of the Lennard-Jones Potential

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We consider a finite chain of particles in one dimension, interacting through the Lennard-Jones potential. We prove the ground state is unique, and approaches uniform spacing in the infinite-particle limit.

KEY WORDS: Crystal; Lennard-Jones potential; infinite-volume ground state.

1. INTRODUCTION

Although there has been notable progress in the understanding of liquid–vapor phase transitions, much less is known about the solid–liquid transition. According to Uhlenbeck,[1] "The basic difficulty lies perhaps in the fact that one does not really understand the existence of regular solids from the molecular forces. Why is it that by taking the minimum of

$$E = \sum_{i<j} \varphi(|\mathbf{r}_i - \mathbf{r}_j|)$$

where $\varphi(|\mathbf{r}|)$ has the usual intermolecular [potential] form, one obtains for large N (strictly for $N \to \infty$) for the positions $\mathbf{r}_i$ of the N points a discrete lattice?"

We will exhibit a mechanism for this phenomenon which works for the Lennard-Jones potential, $\varphi(|\mathbf{r}|) = |\mathbf{r}|^{-12} - |\mathbf{r}|^{-6}$, in one dimension. It is not clear whether the method can be extended to higher dimensions or to quantum mechanics, although there is some hope for the former because of the way the general shape of φ enters the proofs.

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2. NOTATION AND STATEMENT OF RESULTS

The symbols j, k, m, and n always represent integers. Let N be an integer larger than 1, and define

$$I = \{1, 2,..., N\}$$

$$S = \{\{j, j + 1,..., k\} | 1 \leqslant j \leqslant k \leqslant N\}$$

$$T = \{\{1, 2,..., k\} | 2 \leqslant k \leqslant N\}$$

$$\mathbb{R}_+{}^N = \{\mathbf{z} = (z_1,..., z_N) \in \mathbb{R}^N | z_j > 0, j \in I\}$$

If $J \in S$, $|J|$ denotes the cardinality of J.

Consider a system of $N + 1$ "point particles" at positions $x_j \in \mathbb{R}$, where $0 \leqslant j \leqslant N$, $x_0 = 0$, and $x_j < x_k$ for $j < k$. Define $\mathbf{z} = \{z_j | j \in I\}$ by $z_j = x_j - x_{j-1}$, representing the spacing between neighboring particles. V denotes the Lennard-Jones potential, $V(x) = |x|^{-12} - |x|^{-6}$, and the total potential energy of the system is given by

$$E_N(\mathbf{x}) = \frac{1}{2} \sum_{j=0}^{N} \sum_{\substack{k=0 \\ k \neq j}}^{N} V(x_j - x_k) = W_N(\mathbf{z}) = \sum_{n=1}^{N} \sum_{|J|=n} V\left(\sum_{J \in J} z_j\right) \tag{1}$$

We will prove that for fixed N, $E_N(\mathbf{x})$ attains a unique global minimum at $\mathbf{x} = \tilde{\mathbf{x}} = \tilde{\mathbf{x}}(N)$. Then as particles are added one by one at positions x_{-1}, x_{-2}, x_{N+1}, etc. (i.e., to both sides of the chain and in any order such that infinitely many are added to each side), we prove that for $j \in \mathbb{Z}$ fixed, $\tilde{x}_j(N) \to jc$ as $N \to \infty$, where $c = \pi(3{,}714{,}816/1{,}816{,}214{,}400)^{1/6} \simeq 1.119$.

3. PROOF OF RESULTS

Our first result (easily generalized to other potentials and higher dimensions) shows that the forces support an "approximate crystal," a property stronger than H-stability.

Theorem 1. Let $L \in T$, and for $\mathbf{z} \in \mathbb{R}_+{}^N$ consider any coordinates z_j, $j \notin L$, to be fixed and the rest variable. Then $W_N(\mathbf{z})$ assumes a global minimum at one or more points $\tilde{\mathbf{z}} \in \mathbb{R}_+{}^N$, and such a point must satisfy $.99 < \tilde{z}_k < 2^{1/6}$ for $k \in L$.

Proof. Let $\mathbf{z} \in \mathbb{R}_+{}^N$ be fixed throughout this proof, and define $\mathbf{z}^0 \in \mathbb{R}_+{}^N$ by

$$z_j{}^0 = \begin{cases} z_j & \text{if } j \notin L \text{ or } z_j \leqslant 2^{1/6} \\ 2^{1/6} & \text{otherwise} \end{cases}$$

If $z_j > 2^{1/6}$ for some $j \in L$, then $V(z_j^0) < V(z_j)$ and some terms in the expansion (1) of $W_N(\mathbf{z}^0)$ are strictly smaller than the corresponding terms for $W_N(\mathbf{z})$, while all others are equal. This proves $W_N(\mathbf{z}^0) < W_N(\mathbf{z})$ whenever $\mathbf{z}^0 \neq \mathbf{z}$. Next, if $z_j^0 > .99$ for all $j \in L$ define $\mathbf{z}^{00} = \mathbf{z}^0$; otherwise define $\mathbf{z}^{00} \neq \mathbf{z}^0$ as follows. First, for any $\mathbf{v} \in \mathbb{R}_+{}^N$ define $y_j(\mathbf{v}) \in \mathbb{R}_+$, $j = 0, 1,..., N$, by

$$y_j = \begin{cases} 0, & j = 0 \\ v_j + y_{j-1}, & j = 1,..., N \end{cases}$$

Let y_s be the smallest of the $y_j(\mathbf{z}^0)$ for which both $z_j \leqslant .99$ and $j \in L$, and define $(P\mathbf{y})_k \in \mathbb{R}_+$ by

$$(P\mathbf{y})_k = \begin{cases} y_k, & k < s \\ y_{k+1}, & s \leqslant k < N \\ y_N + 2^{1/6}, & k = N \end{cases}$$

Repeat this process if necessary, obtaining $(P^2\mathbf{y})_k$, $(P^3\mathbf{y})_k$, etc., until after $K \leqslant N$ steps we have $(P^K\mathbf{y})_k > .99$ for all k. Finally, define $\mathbf{z}^{00}$ by $z_k^{00} = (P^K\mathbf{y})_k - (P^K\mathbf{y})_{k-1}$, $k \in I$. Now we prove that $W_N(\mathbf{z}^{00}) < W_N(\mathbf{z}^0)$ whenever $\mathbf{z}^{00} \neq \mathbf{z}^0$. Since at each step of the above process the value of W_N is decreased by more than

$$\Delta W \equiv V(b) + 2 \sum_{k=2}^{\infty} V(kb) \qquad \text{for some } b \leqslant .99$$

we need only show that $\Delta W > 0$. To this end note that the smallest $a > 0$ satisfying

$$V(a) - 2 \sum_{j=2}^{\infty} (ja)^{-6} = 0$$

is

$$a = [(2\pi^6)/945 - 1]^{-1/6} > .99$$

Since $V(y) \to \infty$ as $y \to 0$,

$$V(y) - 2 \sum_{j=2}^{\infty} (jy)^{-6} > 0 \qquad \text{for} \quad 0 < y < .99$$

Then, since $V(y) > y^{-6}$, we see that $\Delta W > 0$ as desired. Now using compactness and the continuity of W_N, it follows easily that there is at least one point $\tilde{\mathbf{z}}$ at which W_N attains a global minimum and that such $\tilde{\mathbf{z}}$ must satisfy $.99 < \tilde{\mathbf{z}}_j \leqslant 2^{1/6}$ for $j \in L$. Finally, since $\partial W_N/\partial z_j(\mathbf{z}) \neq 0$ if $z_j = 2^{1/6}$, we have in fact $.99 < \tilde{\mathbf{z}}_j < 2^{1/6}$ for $j \in L$. This ends the proof.

To prove that the above "approximate crystal" is unique for finite N, and becomes perfectly regular as $N \to \infty$, we use the following properties of the Hessian matrix of W_N.

Theorem 2. Let $L \in T$. If $\mathbf{z} \in \mathbb{R}_+{}^N$ satisfies $z_j > .99$ for $j \in I$ and $z_j < 2^{1/6}$ for $j \in L$, and A is the matrix $A_{jk} = \partial^2 W_N/\partial z_j\, \partial z_k(\mathbf{z})$, $j, k \in L$, then:

(a) $A_{jk} < 0$ for $j \neq k$.
(b) A is positive definite.
(c) A^{-1} is positivity preserving.

Proof

$$\partial^2 W_N/\partial z_j\, \partial z_k = \sum_{\substack{J \in S \\ J \supseteq \{j,k\}}} V''\left(\sum_{m \in J} z_m\right) \tag{2}$$

Since in (2), $J \supseteq \{j, k\}$, if $j \neq k$, then $|J| \geqslant 2$ and since all $z_m > .99$, we have $V''(\sum_{m \in J} z_m) < 0$, which proves (a). To prove (b) and (c) we will use the following lemma.

Lemma. $\sum_{j \in L} A_{jk} > 0$, for all $k \in L$.

Subproof

$$\begin{aligned}
&\sum_{j \in L} \partial^2 W_N/\partial z_j\, \partial z_k(\mathbf{z}) \\
&\quad = \partial^2 W_N/\partial z_k{}^2(\mathbf{z}) + \sum_{\substack{j \in L \\ j \neq k}} \partial^2 W_N/\partial z_j\, \partial z_k(\mathbf{z}) \\
&\quad = V''(z_k) + \sum_{n=2}^{N} \sum_{\substack{J \in S;\, J \ni k \\ J \subseteq L;\, |J| = n}} V''\left(\sum_{m \in J} z_m\right) + \sum_{\substack{j \in L \\ j \neq k}} \sum_{n=2}^{N} \sum_{\substack{J \in S;\, J \supseteq \{j,k\} \\ J \subseteq L;\, |J| = n}} V''\left(\sum_{m \in J} z_m\right) \\
&\quad > V''(z_k) - \frac{42}{(.99)^8}\left[\sum_{n=2}^{\infty} n^{-7} + 2\sum_{j=2}^{\infty} \sum_{n=j}^{\infty} n^{-7}\right]
\end{aligned} \tag{3}$$

where we used $z_m > .99$, $V''(y)$ strictly increasing and negative for $y > 1.9$, and $V''(y) > -42y^{-8}$ for $y > 0$. Using $V''(z_k) > V''(2^{1/6}) > 14$, and integral inequalities on the sums, we see that the difference on the RHS of (3) is larger than 0, which proves the lemma.

Now let v_j, $j \in L$, be real variables. Then

$$\begin{aligned}
\sum_{j,k \in L} v_j v_k A_{jk} &= \sum_{j \in L} v_j{}^2 A_{jj} + \sum_{\substack{j,k \in L \\ j \neq k}} v_j v_k A_{jk} \\
&\geqslant \sum_{j \in L} v_j{}^2 A_{jj} + \sum_{\substack{j,k \in L \\ k \neq j}} |v_j|\,|v_k| A_{jk} \\
&\geqslant \sum_{j \in L} v_j{}^2 A_{jj} + \sum_{j \in L} \sum_{\substack{k \in L \\ k \neq j}} [(v_j{}^2 + v_k{}^2)/2] A_{jk} \\
&\geqslant \sum_{j \in L} v_j{}^2 \left(A_{jj} + \sum_{\substack{k \in L \\ k \neq j}} A_{jk}\right) \\
&> 0 \qquad \text{if some } v_j \neq 0, \text{ by the lemma}
\end{aligned}$$

This proves (b). Now assume $v_k > 0$, $k \in L$, and assume $A\mathbf{u} = \mathbf{v}$. We may assume without loss of generality that $|u_j| \geqslant |u_k|$ for $j < k$ since the relevant properties of A are preserved under rearrangement of rows and columns. Assume $u_1 \leqslant 0$. Then

$$0 < v_1 = A_{11}u_1 + \sum_{\substack{j\in L\\ j\neq 1}} A_{1j}u_j \leqslant u_1\Big(A_{11} + \sum_{\substack{j\in L\\ j\neq 1}} A_{1j}\Big)$$

which contradicts the lemma, proving $u_1 > 0$. For induction assume $j \in L$, $j \neq 1$, such that $u_j \leqslant 0$, and $u_k > 0$ for all $1 \leqslant k < j$. Then

$$\begin{aligned} 0 < v_j &= A_{jj}u_j + \sum_{k=1}^{j-1} A_{jk}u_k + \sum_{k=j+1}^{|L|} A_{jk}u_k \\ &< A_{jj}u_j + \sum_{k=j+1}^{|L|} A_{jk}u_k \\ &< u_j\Big(A_{jj} + \sum_{k=j+1}^{|L|} A_{jk}\Big) \end{aligned}$$

which contradicts the lemma, proving the induction, and (c).

The first consequence of Theorem 2 is the following.

Corollary. The global minimum $\tilde{\mathbf{z}}$ of W_N guaranteed by Theorem 1 is unique.

Proof. Theorem 2(b) shows that W_N is convex in the z_k, $k \in L$, if $.99 < z_k < 2^{1/6}$. QED.

Next we must establish control over the dependence on N of the interparticle spacings. Let $L = \{1, 2, \ldots, N-1\}$. For each $z_N > .99$, the Corollary to Theorem 2 shows there is a well-defined function $\tilde{\mathbf{z}}(z_N)$ satisfying $.99 < \tilde{z}_j < 2^{1/6}$ and $\partial W_N/\partial z_j(\tilde{\mathbf{z}}) = 0$ for $j \in L$. Since the determinant $|\partial^2 W_N/\partial z_k\, \partial z_j(\mathbf{z})|$, $j, k \in L$, is not zero, from Theorem 2(b), the implicit function theorem shows that $\tilde{\mathbf{z}}(z_N)$ is differentiable with respect to z_N, and by differentiating the equations $\partial W_N/\partial z_j(\tilde{\mathbf{z}}) = 0$ we see that the $d\tilde{\mathbf{z}}_j/dz_N$ satisfy

$$\sum_{j\in L} [\partial^2 W_N/\partial z_k\, \partial z_j(\tilde{\mathbf{z}})]\, d\tilde{\mathbf{z}}_j/dz_N + \partial^2 W_N/\partial z_N\, \partial z_k(\tilde{\mathbf{z}}) = 0$$

for $k \in L$. But using Theorem 2(a) and (c), we see that $d\tilde{\mathbf{z}}_j/dz_N > 0$ for $j \in L$. As $z_N \to \infty$, the $\tilde{\mathbf{z}}_j(z_N)$ approach the values that minimize W_{N-1}. As z_N comes in from ∞, the $\tilde{\mathbf{z}}_j(z_N)$ decrease monotonically. Somewhere in $(.99, 2^{1/6})$, z_N reaches a value $\tilde{z}_N$ such that $W_N(\tilde{\mathbf{z}}_1(\tilde{z}_N), \ldots, \tilde{\mathbf{z}}_{N-1}(\tilde{z}_N), \tilde{z}_N)$ is the global minimum. Thus, introducing a particle at either end of a finite chain "in the ground state" leads to a new ground-state configuration with all previous spacings decreased. Since each of these spacings are bounded below by .99, if particles are added one by one to both sides, in any order but such that an infinite number are added to each side, then each $\tilde{z}_k$ (k fixed, and now positive or negative to allow adding particles at either end) has a limit c independent of the sequence used and thus independent of k. To compute this limiting, equal spacing we note that for finite N the $\tilde{z}_j$ are the unique solutions in $(.99, 2^{1/6})$ of $\sum_{J\in S;\, J\ni j} V'(\sum_{k\in J} z_k) = 0$. Letting $N \to \infty$, and noting that the corresponding infinite series is uniformly convergent in the z_j, we can let $z_j \to c$ and find that c satisfies

$$\sum_{n=1}^{\infty} nV'(nc) = 0 \tag{4}$$

which can be interpreted as the minimization, with respect to variable c, of $2\sum_{n=1}^{\infty} V(nc)$, the energy per particle of infinitely many equally spaced particles. The solution of (4) is easily seen to be $[2\zeta(12)/\zeta(6)]^{1/6} = \pi(3{,}714{,}816/1{,}816{,}214{,}400)^{1/6}$, where ζ is Riemann's zeta function.

We summarize our results as follows.

Theorem 3. For fixed N, $E_N(\mathbf{x})$ attains a unique global minimum, at $\mathbf{x} = \tilde{\mathbf{x}}$. As infinitely many particles are added one by one to both sides of the chain, in any order, then for fixed $j \in \mathbb{Z}$, $\tilde{x}_j \to jc$ as $N \to \infty$, where $c = \pi(3{,}714{,}816/1{,}816{,}214{,}400)^{1/6}$. (We note without proof that for finite N, the unique ground state is actually the unique state of static equilibrium.)

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REFERENCE

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