

A First-Order Phase Transition between Crystal Phases in the Shift Model

Francesco Nicolò^{1,2} and Charles Radin^{1,3}

Received January 26, 1982

We describe rigorously a many-body model of interacting classical particles exhibiting the following behavior at zero temperature: as the pressure varies through a critical value, the system goes through a first-order phase transition between different crystal phases. Moreover, at the critical pressure the system is demonstrably a mixture of the two phases.

KEY WORDS: Phase transition; crystal; ground state.

1. INTRODUCTION

It remains at heart obscure why all forms of matter tend to be crystalline rather than amorphous at low temperature. After all, a crystalline configuration is rarely if ever observed⁽¹⁾ for *small* clusters of molecules (less than 100, say); it must be a question of extending patterns to *large* clusters that forces the crystalline symmetry. This is one of the major unsolved problems of condensed matter physics.⁽²⁾

Most of the effort on this problem (see Ref. 3 and references therein) has centered on the molecular-bonded solids, using classical mechanics and Lennard–Jones-type forces. Since even the various close-packed crystals yield extremely close molar energies, it has been necessary to concentrate on models in one and two dimensions; since Mermin's theorem⁽⁴⁾ indicates a lack of long range order for temperature $T > 0$ in these dimensions, one is lead to investigate the case $T = 0$.

Below we describe rigorously a many-body model of interacting classical particles exhibiting the following behavior at low (zero) temperature: as

¹ Mathematics Department, The University of Texas, Austin, Texas 78712.

² Permanent address: Istituto di Matematica, Università di Roma; INFN, Rome, Italy.

³ Supported in part by NSF Grant No. MCS81-01596.

the pressure varies through a critical value, the system goes through a first-order phase transition between different crystal phases. Moreover, at the critical pressure the system is demonstrably a mixture of the two phases. (For a general reference see Ref. 2.)

Our model (which we call the shift model) is one dimensional with interaction potential:

$$\Phi(r) = \begin{cases} +\infty, & 0 \leq r < 0.96 \\ -100r + 97.8, & 0.96 \leq r \leq 0.98 \\ -r + 0.78, & 0.98 \leq r \leq 2 \\ 1.16r - 3.54, & 2 \leq r \leq 3 \\ 0.1r - 0.36, & 3 \leq r \leq 3.6 \\ 0, & 3.6 \leq r \end{cases}$$

Note that the range of Φ is less than $4(0.96)$ so each particle interacts with at most three particles on each side of it on the line. (The graph of Φ is continuous for $r > 0.96$, and composed of line segments.)

Throughout this paper we assume a fixed number $N \geq 11$ of particles in the system. The total (potential) energy $E^T(x)$ of a configuration (i.e., set of particle positions) $x = \{x_1, x_2, \dots, x_N\}$, $x_{k+1} > x_k$, depends only on the "spacing sequence" $\{x_2 - x_1, x_3 - x_2, \dots, x_N - x_{N-1}\}$ and can be decomposed:

$$E^T(x) = (1/4) \sum_{j=1}^{N-4} E_j(x) + C(x)$$

where

$$\begin{aligned} E_j(x) = & [\Phi(x_{j+1} - x_j) \\ & + \Phi(x_{j+2} - x_{j+1}) + \Phi(x_{j+3} - x_{j+2}) + \Phi(x_{j+4} - x_{j+3})] \\ & + (4/3)[\Phi(x_{j+2} - x_j) + \Phi(x_{j+3} - x_{j+1}) + \Phi(x_{j+4} - x_{j+2})] \\ & + 2[\Phi(x_{j+3} - x_j) + \Phi(x_{j+4} - x_{j+1})] \end{aligned}$$

and $C(x)$ (due to undercounting the nine interactions involving the three particles at each end) is bounded as $N \rightarrow \infty$. (When considering one E_j we also denote $\{x_j, x_{j+1}, x_{j+2}, x_{j+3}, x_{j+4}\}$ by x .) Note that $C(x) \equiv 0$ if periodic boundary conditions are used.

We are concerned with low-temperature behavior. The statistical ensemble (the "pressure ensemble"⁽²⁾) corresponding to fixed pressure p and inverse temperature β has density $\exp\{-\beta[E^T(x) + pV^T]\}$, where V^T is the (variable) volume: $V^T \geq x_N - x_1$. Therefore at zero temperature the ensemble (i.e., probability measure) is concentrated on those configurations x which minimize $E^T(x) + pV^T$, where now $V^T = V^T(x) = x_N - x_1$. Our main task is thus to minimize $E^T(x)$ (with variable volume constraint). It is

noteworthy that we can accurately approximate such a minimizing configuration by instead minimizing each $E_j(x)$ and noting that the N -particle configurations which do this can be chosen to be "compatible" in the sense that they minimize $E_j(x)$ for all j simultaneously. We minimize each $E_j(x)$ with x subject to the variable constraint of given volume $V_j(x) \equiv x_{j+4} - x_j$.

2. ESTIMATES

First we note from simple considerations that to minimize $E_j(x) + pV_j(x)$, $p \geq 0$ fixed, we need only consider x such that $3.84 \leq V_j(x) \leq 4$. It is convenient to reparametrize volume by $w = 4 - V_j$, $0 \leq w \leq 0.16$. Define

$$\tilde{E}(w) = \min [E_j(x) \mid x_{j+4} - x_j = 4 - w]$$

$$F(p) = \min [\tilde{E}(w) + p(4 - w) \mid 0 \leq w \leq 0.16]$$

and let $E_{eq}(w)$ be the value of $E_j(x)$ when the x_k are equally spaced, $x_{k+1} - x_k = 1 - w/4$. In computing $\tilde{E}(w)$ we will consider separately the intervals $0 \leq w \leq 0.08$ and $0.08 \leq w \leq 0.16$, and we begin with the former.

It is easy to check that for $0 \leq w \leq 0.08$, $E_{eq}(w) = E_{eq}(0) - 0.48w$. To compute $\tilde{E}(w)$ we consider a configuration of five equally spaced particles with $x_{j+4} - x_j = 4 - w$ and compute the change in energy under arbitrary displacement of x_{j+1} , x_{j+2} , x_{j+3} . Let $E_{a,b,c}$ denote the value of $E_j(x)$ when x_{j+1} (resp. x_{j+2} , x_{j+3}) is increased by the amount a (resp. c, b) from its equal-spacing position; a, b, c are possibly negative. It is easy to see from force considerations that in any minimum configuration ($0 \leq w \leq 0.08$) no two particles are closer than 0.98 and also that $|c| \leq w/2$. There are three basic cases to consider: $a \geq b \geq 0$, $b \geq a \geq 0$ and $a \geq 0 \geq b$. (The case $a < 0 \leq b$ cannot lead to a minimum unless $a = b = 0$.) Assuming $a \geq b \geq 0$ one can show that the following inequalities are sharp: For $0 \leq w \leq 0.22/85$, $E_{a,b,c} \geq E^{(1)}(w) \equiv E_{eq}(w) + 1.06(w - 0.04) + 1.7w/3$ (with equality when $w = 0$ only if $a = b = 0.02$, $c = 0$), and for $0.22/85 \leq w < 0.08$, $E_{a,b,c} \geq E^{(2)}(w) \equiv E_{eq}(w) + 2.96(w/2 - 0.04)/3$ (with equality when $w = 0.08$ only if $a = b = c = 0$).

Assuming $b \geq a \geq 0$, one can show that the following inequalities are sharp: For $0 \leq w \leq 0.02$, $E_{a,b,c} \geq E^{(3)}(w) \equiv E_{eq}(w) + 1.06(2w - 0.04)$ (with equality when $w = 0$ only if $a = b = 0.02$, $c = 0$), and for $0.02 \leq w < 0.08$, $E_{a,b,c} \geq E_{eq}(w)$ (with equality when $w = 0.08$ only if $a = b = c = 0$).

Finally, assuming $a \geq 0 \geq b$ one can show that the following inequality is sharp: $E_{a,b,c} \geq E^{(2)}(w)$ (with equality when $w = 0.08$ only if $a = b = c = 0$.) Note that $E^{(3)}(w) > E^{(1)}(w)$ for $0 < w \leq 0.08$, $E^{(2)}(w) > E^{(1)}(w)$ for $0 \leq w < 0.22/85$ and $E^{(2)}(w) < E^{(1)}(w)$ for $0.22/85 < w \leq 0.08$. Thus $\tilde{E} = E^{(1)}$ on $[0, 0.22/85]$ and $\tilde{E} = E^{(2)}$ on $[0.22/85, 0.08]$.

Next we compute $\tilde{E}(w)$ for $0.08 \leq w \leq 0.16$. It is easy to check that $E_{\text{eq}}(w) = E_{\text{eq}}(3.92) + 98.52(w - 0.08)$. Using the obvious constraint $0.96 \leq x_{k+1} - x_k \leq 0.98$ we find the sharp inequalities: For $0.08 \leq w \leq 0.12$, $E_{a,b,c} \geq E^{(4)}(w) \equiv E_{\text{eq}}(w) - 1.48(w - 0.08)/3$ (with equality when $w = 0.08$ only if $a = b = c = 0$) and for $0.12 \leq w \leq 0.16$, $E_{a,b,c} \geq E^{(5)}(w) \equiv E_{\text{eq}}(w) - 1.48(0.16 - w)/3$ (with equality when $w = 0.16$ only if $a = b = c = 0$.) Therefore $\tilde{E} = E^{(4)}$ on $[0.08, 0.12]$ and $\tilde{E} = E^{(5)}$ on $[0.12, 0.16]$.

Now consider $F(p)$, using the facts

$$\frac{d}{dw} E^{(1)}(w) = 4.34/3$$

$$\frac{d}{dw} E^{(2)}(w) = 0.04/3$$

$$\frac{d}{dw} E^{(4)}(w) = 294.08/3$$

$$\frac{d}{dw} E^{(5)}(w) = 297.04/3$$

For $p = 0$ it is clear that $F(0) = \tilde{E}(0)$, and $E_j(x) = F(0)$ only for the spacing sequences

$$\{0.98, 1.02, 0.98, 1.02\} \text{ or } \{1.02, 0.98, 1.02, 0.98\} \quad (1)$$

To determine $F(p)$ for $p > 0$ we first use the fact that as a function of w , $\tilde{E}$ is concave downward on $[0, 0.08]$. This is the feature of our model producing the discontinuous decrease of volume with increasing pressure since it follows that there is a critical value p_c of p (easily seen to be $p_c = 0.05$) such that for $0 \leq p < p_c$, $F(p) = \tilde{E}(0) + 4p$ with $F(p) = E_j(x) + pV_j(x)$ only for $V_j(x) = 4$ and either of the "shifted" spacing sequences in (1), while for $p_c < p < 297.04/3$, $F(p) = E_j(x) + pV_j(x)$ only for $V_j(x) = 3.92$ and equal spacing, of size 0.98.

For each p , $0 \leq p < 297.04/3$, $p \neq p_c$, define

$$V(p) = \begin{cases} 4, & 0 \leq p < p_c \\ 3.92, & p_c < p < 297.04/3 \end{cases}$$

Next note that crude estimates show that if $V_j(x) = 4 + w$, $0 \leq w \leq 1$, then $E_j(x) \geq E_{\text{eq}}(w) - 0.0424 + 1.64w/3$. Combining this with our results on $\tilde{E}(w)$, we see that for small w of either sign: if $V_j(x) = 4 + w$, $E_j(x) - \tilde{E}(0) \geq 1.64|w|/3$, and if $V_j(x) = 3.92 + w$, $E_j(x) - \tilde{E}(0.08) \geq 0.04|w|/3$.

3. CONCLUSION

Thus from the calculations above we immediately conclude that there exist finite constants C_k independent of N such that if for a system of N

particles $x = x(N)$ minimizes $E^T(x) + pV^T(x)$: (a) $|E^T(x(N)) - (N/4)\tilde{E}(4 - V(p))| < C_1$; (b) $|V^T(x(N)) - NV(p)/4| < C_2$; (c) for large N , $x(N)$ "looks like" the appropriate crystal for that pressure, i.e., given $\epsilon > 0$, at most $C_3/\epsilon N$ blocks of five consecutive particles can differ from the appropriate perfect crystal block by more than ϵ (measured with the Euclidean norm in $\mathbb{R}^5$.)

We thus have the existence and value of the asymptotic energy per particle and volume per particle:

$$e(p) = \lim_{N \rightarrow \infty} E^T(x(N))/N = (1/4)\tilde{E}(4 - V(p))$$

$$= \begin{cases} E_{\text{eq}}(0)/4 - 0.0106, & 0 \leq p < p_c \\ E_{\text{eq}}(0)/4 - 0.0096, & p_c < p < 297.04/3 \end{cases}$$

$$v(p) = \lim_{N \rightarrow \infty} V^T(x(N))/N = V(p)/4$$

$$= \begin{cases} 1, & 0 \leq p < p_c \\ 0.98, & p_c < p < 297.04/3 \end{cases}$$

At $p = p_c$ the volume is no longer constrained. It follows immediately from our calculations of $\tilde{E}$ that there exists a finite constant C_4 independent of N such that if $x(N)$ is a configuration minimizing $E^T(x) + p_c V^T(x)$, and $v = V^T(x(N))/N = aV(p_c - 0) + (1 - a)V(p_c + 0)$ for some a in $[0, 1]$, then: (d) For large N , $x(N)$ "looks like" a mixture of the two crystal phases, i.e., given $\epsilon > 0$ at most $C_4/\epsilon N$ blocks of five consecutive particles differ from one or the other perfect crystal block by at most ϵ . This implies that $x(N)$ consists of a small number of long chains of essentially perfect crystals of the two types, and, to obtain the proper volume, the number of blocks B_L of the low-pressure phase and B_H of the high-pressure phase must be in the proportion: $B_L/B_H = a/(1 - a)$.

Finally we note that simple force estimates show that sufficiently small changes in the interaction potential, including smoothing its corners, would preserve the first-order transition while making the volume a strictly decreasing function of $p \neq p_c$; we expect they would also preserve the crystal phase structure, though this seems harder to prove.

ACKNOWLEDGMENTS

We gratefully acknowledge useful discussions with Clifford Gardner and William McCormick.

REFERENCES

1. J. Farges, B. Raoult, and G. Torchet, *J. Chem. Phys.* **59**:3454 (1973).
2. G. E. Uhlenbeck, in *Fundamental Problems in Statistical Mechanics, II*, E. G. D. Cohen, ed (John Wiley, New York, 1968).
3. C. Radin, Crystalline symmetry and surface tension, *Physica A*, to appear.
4. N. D. Mermin, *Phys. Rev.* **176**:250 (1968); **B20**:4762 (1979).