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How a solid can be turned into a gas without passing through a first-order phase transformation

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Recent calculations of the absolute free energy of a solid using molecular dynamics and Monte Carlo simulated data employ a “thermodynamic” path which is numerically indistinguishable from a path which connects a solid and an ideal gas. No first-order phase transition is observed on this path. We present an interpretation of this type of path, we identify a particular path along which the numerical uncertainty in calculating the free energy is minimized, and we report numerical studies on a Lennard-Jones system which support the surprising proposition that there is such a singularity-free path.

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Evaluation of an absolute free energy by direct numerical integration over phase space is not possible because of the high dimensionality of the integrals, but the free energy change along a path in thermodynamic state space can be evaluated by molecular dynamics (MD) [1] and Monte Carlo (MC) [2–5] simulation [6]. At a molecular level a path is simply a one-parameter family of Hamiltonians $H(\lambda)$. Since Hamiltonians need only be imagined, simulators have access to a greater variety of paths than experimenters.

Consider the path associated with the family of Hamiltonians

$$H(\lambda) = \sum_{i=1}^N \frac{p_i^2}{2m} + \lambda \sum_{i<j} V(r_{ij}) + (1-\lambda) \sum_{i=1}^N U(r_i). \quad (1)$$

$H(0)$ describes N noninteracting particles in a one-particle external field $U(\mathbf{r})$ and $H(1)$ describes a system of particles interacting through pairwise additive forces. If $A(\lambda)$ is the free energy of the thermodynamic state associated with each $\lambda \in [0,1]$, then [6]

$$\partial A(\lambda)/\partial \lambda = \langle V-U \rangle_\lambda \quad (2)$$

is the canonical ensemble expectation of the difference between the two-particle and one-particle potential energy functions in state λ , a mechanical property which can be evaluated by simulation at each λ . If $\langle V-U \rangle_\lambda$ is nonsingular, the free energy difference along this path can be determined from

$$A(1) - A(0) = \int_0^1 \frac{\partial A(\lambda)}{\partial \lambda} d\lambda. \quad (3)$$

Since no two-particle interactions are present in the $\lambda=0$ state, explicit integration over phase space gives an absolute (third law) value for $A(0)$ [7],

$$A(0) = -Nk_B T \ln \left\{ (e/N\Lambda^3) \int_V d\mathbf{r} \exp[-U(\mathbf{r})/k_B T] \right\}. \quad (4)$$

If N/V is chosen so that the $\lambda=1$ state will be a solid, (3) and (4) will identify the absolute free energy for the solid. We address two important questions about this path. (i) What external field $U(\mathbf{r})$ should be used? (ii) Where is the first-order phase transition?

(i) The choice of $U(\mathbf{r})$ refers to the practical question: Along what path can the integral in (1) be evaluated with the least statistical uncertainty? Integrating (2) by parts gives

$$\begin{aligned} A(1) - A(0) &= A'(1) - \int_0^1 d\lambda \lambda A''(\lambda) \\ &= \langle V - U \rangle_{\lambda=1} + \frac{1}{k_B T} \int_0^1 d\lambda \lambda [\langle (V - U)^2 \rangle_{\lambda} \\ &\quad - \langle V - U \rangle_{\lambda}^2] \\ &= \langle V - U \rangle_{\lambda=1} + \Delta F. \end{aligned} \quad (5)$$

There is no statistical uncertainty in calculating $A(0)$. If the solid state of interest ($\lambda = 1$) is carefully characterized, then ΔF will be the principal source of statistical uncertainty in applying (3).

Since ΔF in (5) is a weighted integral over the variance of $(V - U)$, it must be positive definite and there must be a $U(\mathbf{r})$ field for which ΔF is minimized, i.e., a *best* $U(\mathbf{r})$. This is the $U(\mathbf{r})$ for which

$$\begin{aligned} 0 &= \frac{\delta \Delta F}{\delta U(\mathbf{r})} = \frac{1}{k_B T} \frac{\delta}{\delta U(\mathbf{r})} \int_0^1 d\lambda \lambda [\langle (U - V)^2 \rangle_{\lambda} - \langle U - V \rangle_{\lambda}^2] \\ &= \frac{\delta}{\delta U(\mathbf{r})} [A(1) - A(0) - A'(1)] \\ &= \frac{\delta}{\delta U(\mathbf{r})} [-A(0) - \langle V - U \rangle_{\lambda=1}] \\ &= \rho_{\lambda=1}(\mathbf{r}) - \rho_{\lambda=0}(\mathbf{r}). \end{aligned} \quad (6)$$

The fluctuations are thus minimized by the $U(\mathbf{r})$ field which produces, in the $\lambda = 0$ state, the *same* density as the target solid. If $\rho_S(\mathbf{r}) = \rho_{\lambda=1}(\mathbf{r})$ is this solid density, the required $U(\mathbf{r})$ has the form

$$U(\mathbf{r}) = -k_B T \ln \rho_S(\mathbf{r}) + \text{const.} \quad (7)$$

This is a physically attractive result: the statistically optimal path is that which connects a solid to a system in a one-particle field with the same $\rho_S(\mathbf{r})$.

Simulations along paths which are *numerically* indistinguishable from (1) have already been performed. Lutsko, Wolf, and Yip (LWY) [1], for example, evaluated the free energy of simple solids using the path

$$H_{\text{LWY}}(\lambda) = \sum_{i=1}^N \frac{p_i^2}{2m} + \lambda \sum_{i < j} V(r_{ij}) + (1 - \lambda) \sum_{i=1}^N \frac{1}{2} \kappa (r_i - r_{i0})^2, \quad (8)$$

a variant of a path originally proposed by Frenkel and Ladd (FL) [2]. The $\lambda = 0$ state has particle i bound harmonically to lattice site r_{i0} , a system described by FL as an *Einstein crystal*. There is a large formal difference between (1) and (8): (8) replaces the two-particle potential $V(r_{12})$ with an N -particle potential which binds each particle harmonically to a *particular* lattice site while (1) replaces $V(r_{12})$ with a one-particle potential $U(\mathbf{r})$. But these paths are indistinguishable in a low temperature simulation where the prob-

ability of finding a particle between two lattice sites is always very low: While (1) allows particles in principle to change lattice positions this never occurs in practice. In fact, LWY [1] observed that the numerical uncertainty associated with their thermodynamic integration was quite sensitive to the choice of the force constant κ in (8). Result (7) explains this observation and gives a rule for selecting the optimum potential.

(ii) If we replace $U(\mathbf{r})$ in $H(0)$ with a scaled $\mu U(\mathbf{r})$, $\mu = 1 \rightarrow 0$ completes the conversion of the solid into a textbook ideal gas. Along this path there is no singularity. But all laboratory paths which connect a solid and a gas pass through at least one first-order phase transition. Is there a singularity along path (1)?

Strictly speaking, $\langle V - U \rangle_{\lambda=0}$ should diverge because there is a small chance that the repulsive cores of the particles will overlap. The probability of this event is extremely small, however, and in neither our simulation nor that of LWY [1] was such a divergence observed. Since $A(\lambda=0)$ is not singular, this singularity is an artifact of the path. Mezei [8] has shown how this type of divergence can be avoided by altering the path when λ gets very close to zero. In any case, no singularity arising from *cooperative* phenomena can appear as $\lambda \rightarrow 0$. All real measurements and simulations are performed on finite samples, which means that certain long wavelength fluctuations are suppressed. We have taken $\rho_S(\mathbf{r})$ from the finite sample actually simulated in order to avoid a discontinuity at $\lambda = 1$ due to a change in the constraint on these fluctuations.

It was implicitly *assumed* in the simulations of LWY [1] and FL [2] that no singularity was present on the $\lambda = 1 \rightarrow 0$ path. This absence of a singularity is more plausible from the perspective of density functional theory, which guarantees that we could define a thermodynamic path by prescribing $\rho(\mathbf{r})$ rather than $U(\mathbf{r})$. If we define the path by $\rho(\mathbf{r}) = \rho_S(\mathbf{r})$ then we eliminate *a priori* the usual signature of a first-order phase transition, an abrupt change in $\rho(\mathbf{r})$, while optimizing the statistics as required by (6). In our numerical simulation (described below) using path (1) and (7), we found that $\rho_{\lambda}(\mathbf{r})$ is a continuous function of λ which remains close to $\rho_S(\mathbf{r})$ at all λ .

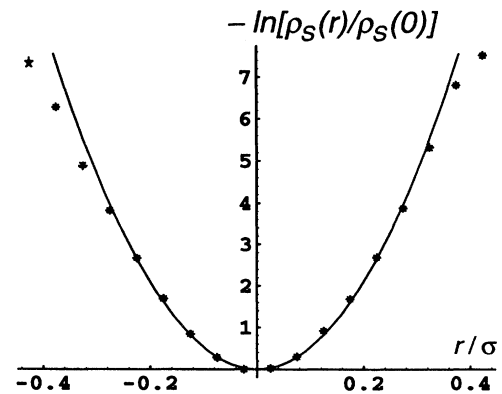


FIG. 1. $-\ln[\rho_S(r)/\rho_S(0)]$ vs r along a crystal axis (points marked +) and along a bisector of two crystal axes (points marked \times). The solid curve is the parabolic representation $U(r)/k_B T = 52.3(r/\sigma)^2$ for the one-particle potential used in the simulation.

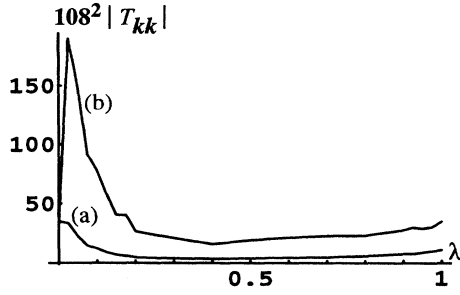


FIG. 2. $|T_{kk}| \times 108 \times 108$ vs λ for k along (a) the [111] and (b) the [400] directions in reciprocal lattice space.

The evidence indicates that no actual discontinuity in $\rho_\lambda(\mathbf{r})$ is encountered along the path (1) and (7). It remains possible, however, that this path is sufficiently close to a path with a discontinuity that there would be singularities associated with *second-order* distribution functions. Perturbative and variational constructions of solids out of fluid states based on density functional theory [9,10] implicitly contain such a singularity, for the solidlike $\rho(\mathbf{r})$ solutions arise by bifurcation out of fluid solutions and there is an associated mechanical singularity (unobserved in real systems) [11,12]. To test whether such a singularity is present on path (1) with external field (7) we have determined the free energy of a face centered cubic (fcc) solid by making a constant N, T, V MD simulation [13] of 108 Lennard-Jones particles at a temperature $T = 0.5\epsilon/k_B$ and density $0.85\sigma^{-3}$ (where the melting temperature is $0.585\epsilon/k_B$ [14]).

With fcc symmetry $\rho_S(\mathbf{r})$ [and hence $U(\mathbf{r})$] must be isotropic near lattice sites. Figure 1 shows $-\ln[\rho_S(\mathbf{r})/\rho_S(0)]$ (the origin is on a lattice site) along two directions in the $\lambda = 1$ state. Even at large displacements little anisotropy is apparent in $\rho_S(\mathbf{r})$ so $U(\mathbf{r})$ was taken to be isotropic. In fact, nonparabolic behavior is only apparent for displacements $|\Delta\mathbf{r}| > 0.325\sigma$, an event with probability < 0.001 since the rms displacement is 0.097σ at this T . Thus taking $U(\mathbf{r})$ to be harmonic near lattice sites is a good approximation. As particle interchanges between lattice sites (a jump of $|\Delta\mathbf{r}| = 1.1848\sigma$) are not observed, a simulation in $U(\mathbf{r})$ is *numerically* indistinguishable from a simulation in a potential which binds distinct particles to distinct lattice sites, i.e., an *Einstein solid* in the sense of [1,2,4,5]. In fact, we used the N -particle field

$$U_N = \sum_n \frac{1}{2} \kappa (\mathbf{r}_n - \mathbf{r}_{n0})^2 \quad (9)$$

in our simulation as this simplified the coding.

Simulation at each λ enabled us to determine $\rho_\lambda(\mathbf{r})$ and the pair distribution function $\rho_\lambda^{(2)}(\mathbf{r}, \mathbf{r}')$. There is only a small variation of $\rho_\lambda(\mathbf{r})$ with λ . The maximum deviation of the [111] Fourier amplitude of $\rho_\lambda(\mathbf{r})$ from that of $\rho_S(\mathbf{r})$, for example, is only 6%. To test for the existence of nearby phases or bifurcation off the phase nominally present, we examined the linear response of $\rho(\mathbf{r})$ to a perturbing single-particle field $\delta U(\mathbf{r})$. This is characterized by the pair distribution function,

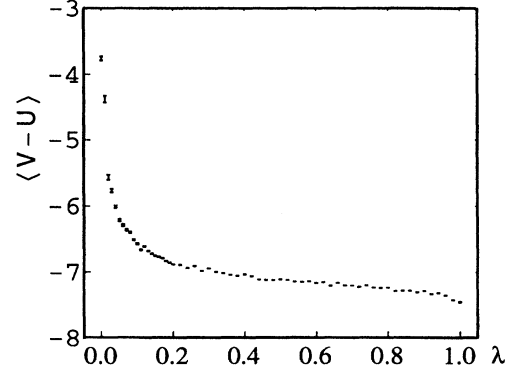


FIG. 3. The integrand $\langle V - U \rangle$ in (2) vs λ on the integration path in (3). The error bars represent \pm twice the variance of the observations.

$$\delta\rho(\mathbf{r}) = \int d\mathbf{v} [\rho^{(2)}(\mathbf{r}, \mathbf{r}') + \rho(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}')] \delta U(\mathbf{r}'), \quad (10)$$

or, in a Fourier representation,

$$\delta\rho_{\mathbf{k}} = \sum_l T_{kl} \delta U_l$$

with

$$T_{kl} = \int \int d\mathbf{v} d\mathbf{v}' [\rho^{(2)}(\mathbf{r}, \mathbf{r}') + \delta(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}) - \rho(\mathbf{r})\rho(\mathbf{r}')] e^{-i(\mathbf{k}\cdot\mathbf{r} - l\cdot\mathbf{r}')}.$$

The presence of mechanical instability or bifurcation is signaled by a large response, T_{kl} [11,12]. For each \mathbf{k} we found that $|T_{kl}|$ is largest for $l \approx \mathbf{k}$ and the λ dependence shows no singularity. Figure 2 shows plots of $|T_{kk}|$ vs λ for \mathbf{k} in the [111] and [400] directions. The maximum value occurs at $\lambda = 0.025$, i.e., in the weakly interacting gas state. Large values for $|T_{kl}|$ which signal singular behavior are not observed.

The values of $\partial A / \partial \lambda = \langle V - U \rangle_\lambda$ plotted in Fig. 3 show a smooth function of λ . The absolute (third law) free energy calculated by evaluating (3) is $A(1) = -8.148\epsilon$ at $\rho = 0.85\sigma^{-3}$, $T = 0.5\epsilon/k_B$ and -8.667ϵ at $\rho = 1.0\sigma^{-3}$, $T = 0.5\epsilon/k_B$. For the data in Fig. 3, $A(1) - A(0) = -6.876\epsilon$. Singer [3] found $A(1) = -8.635\epsilon$ at $\rho = 0.9989\sigma^{-3}$, $T = 0.5008\epsilon/k_B$.

The surprising result that emerges from this picture is that, at least for simple molecular systems, a solid *can* be turned continuously into an ideal gas if one chooses a “thermodynamic” path along which the pair potential is replaced by a single-particle potential that keeps the single-particle density $\rho(\mathbf{r})$ fixed. In fact, the numerical accuracy of the thermodynamic integration is optimized along this path and the magnitude of the free energy change along this path is not large.

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