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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  $\lambda$ , a *mechanical* property which can be evaluated by simulation at each  $\lambda$ . 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  $\Delta F$  will be the principal source of statistical uncertainty in applying (3).

Since  $\Delta F$  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  $\Delta F$  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  $\kappa$  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  $\lambda$  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  $\lambda$  which remains close to  $\rho_S(\mathbf{r})$  at all  $\lambda$ .

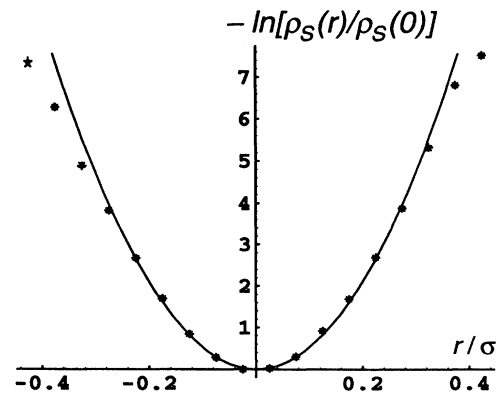


FIG. 1.  $-\ln[\rho_S(\mathbf{r})/\rho_S(0)]$  vs  $r$  along a crystal axis (points marked +) and along a bisector of two crystal axes (points marked  $\times$ ). The solid curve is the parabolic representation  $U(\mathbf{r})/k_B T = 52.3(r/\sigma)^2$  for the one-particle potential used in the simulation.

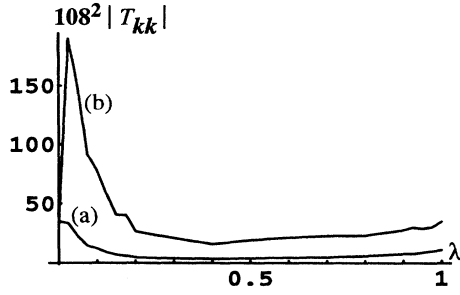


FIG. 2.  $|T_{kk}| \times 108 \times 108$  vs  $\lambda$  for  $k$  along (a) the [111] and (b) the [400] directions in reciprocal lattice space.

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  $0.097\sigma$  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  $\lambda$  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  $\lambda$ . 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,

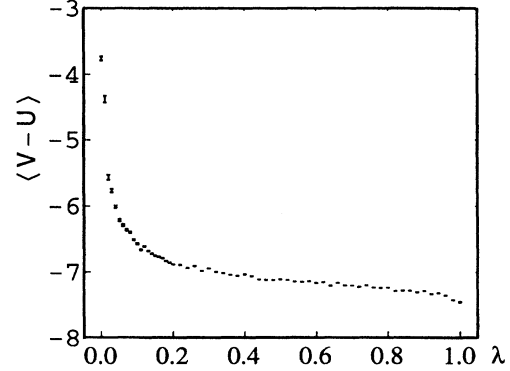


FIG. 3. The integrand  $\langle V - U \rangle$  in (2) vs  $\lambda$  on the integration path in (3). The error bars represent  $\pm$  twice the variance of the observations.

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

or, in a Fourier representation,

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

with

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

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  $\mathbf{l} \approx \mathbf{k}$  and the  $\lambda$  dependence shows no singularity. Figure 2 shows plots of  $|T_{kk}|$  vs  $\lambda$  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  $\lambda$ . 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  $-8.667\epsilon$  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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