Dynamic Long-Range Forces and Z Branches at Phase Transitions

B. A. Huberman and Richard M. Martin
Xerox Palo Alto Research Center, Palo Alto, California 94304
(Received 3 May 1977)

We show that the critical dynamics of dense pseudospin systems interacting via retarded long-range forces (e.g., acoustic phonons) gives rise to the appearance of a Z branch in the central-peak dispersion which should be observable by light-scattering techniques. The evolution of an initially nonconserved quantity towards a hydrodyamic regime leads to liquidlike behavior of the solid for a range of wave vectors.

There exist a number of solids that posses local relaxational degrees of freedom,[1] such as hopping atoms in superionic conductors,[2] rotation of molecules in plastic crystals,[3] and degenerate electronic ground-state Jahn-Teller systems.[4-6] These features are similar to orientational modes in molecular liquids[7] but here the existence of a regular lattice allows for a description in terms of pseudospins[2,4,5] associated with each lattice point. The interactions that the lattice provides between the pseudospins lead not only to their ordering[8] at a critical temperature T_c but also to marked changes in the dynamics of the relaxation modes as T_c is approached from above.

In this Letter we study the critical dynamics of pseudospins coupled via long-wavelength acoustic phonons. The results are of interest because of the following: (1) Whenever coupling is allowed by symmetry, low-frequency acoustic phonons always are renormalized by their interactions with the pseudospins. (2) The retarded long-range interactions between pseudospins provided by the acoustic phonons lead to anomalous critical dynamics not present in either Ising-like systems[4,9] or Ginzburg-Landau ones,[10] since the interactions in these models are always instantaneous. In particular, we find that the acoustic modes become completely overdamped over a range of wave vectors $\vec{k}$ although they remain well defined for $k \to 0$ and large k. In other words there is a range of wave vectors for which the solid displays liquid behavior. (3) The resulting overdamped modes contribute to a "Z" branch in the dispersion curve for the central-peak width which is accessible by light-scattering techniques. As we show, the behavior of these systems displays in a simple and striking way how the dynamics of an originally nonconserved quantity evolves into hydrodynamic-like modes. Finally, the results are applied to the superionic conductor[2] $RbAg_4I_5$ and to the cooperative Jahn-Teller system[4-6] $TmVO_4$.

We consider a system with local degrees of freedom represented by a pseudospin density $n_0 s(\vec{r})$ having a given symmetry representation and an equilibrium value $\bar{s}$. n_0 is the density of relaxing units. In the absence of any couplings other than those to the lattice thermal reservoir, $\bar{s}$ is nonconserved[10] and its time dependence is given by a local equation of the form

$$ds/dt = -\Gamma_0(s - \bar{s}), \tag{1}$$

with Γ_0 a relaxation rate which has an Arrehnius behavior. We consider here the case of acoustic phonons providing interactions between the pseudospins. In this case the Hamiltonian of the system can be written as

$$H = \sum_{\vec{k}} [\tfrac{1}{2}\rho(-\omega^2 + v_s^{02}k^2)Q^2(\vec{k}, \omega) + n_0 kAQ(\vec{k}, \omega)s(\vec{k}, \omega)], \tag{2}$$

where Q is the atomic displacement, ρ the mass density, v_s^0 the appropriate unrenormalized sound velocity, $\vec{k}$ the wave vector, and A the coupling constant. Here $A(kQ)$ is the change in chemical potential per pseudospin[2] caused by the strain kQ. This pervasive Hamiltonian appears as the starting point in many investigations of pseudospin ordering and dynamics.[1-5,9,11]

Marginal dimensionality considerations for acoustic-mode softening show that $d^* = 2$ or $d^* = 3$, depending upon whether the particular phonons are confined to either lines or planes of the Brillouin zone.[12] Therefore a mean-field-theory treatment of the dynamics will be appropriate for three-dimensional systems, provided one remembers that logarithmic corrections will appear very near T_c in the case $d^* = 3$.[13]

The equations of motion that result from the Hamiltonian of Eq. (2) together with the relaxa-

tion equation for the noninteracting pseudospins [Eq. (1)] can be written in the form[2,5]

$$(\Gamma_0 - i\omega)s(\vec{k}, \omega) + (\Gamma_0 kA/k_B T)Q(\vec{k}, \omega) = 0, \quad (3)$$

$$(v_s^{02}k^2 - \omega^2)Q(\vec{k}, \omega) + (n_0 kA/\rho)s(\vec{k}, \omega) = 0, \quad (4)$$

where k_B is the Boltzmann constant, and T the temperature. In the spirit of linear-response theory, Eqs. (3) and (4) can be cast in a form that is more useful for obtaining quasielastic scattering cross sections, i.e.,

$$\chi_s^{-1}s(\vec{k}, \omega) + kAQ(\vec{k}, \omega) = 0 \quad (5a)$$

and

$$\chi_Q^{-1}Q(\vec{k}, \omega) + (n_0/\rho)kAs(\vec{k}, \omega) = 0, \quad (5b)$$

with $\chi_s = [k_B T(1 - i\omega/\Gamma_0)]^{-1}$ and $\chi_Q = (v_s^{02}k^2 - \omega^2)^{-1}$, the decoupled spin and phonon susceptibilities, respectively. One should note that Eqs. (5a) and (5b) are quite general and retain their form even in the case where additional couplings are included in the χ's.

The dispersion relation for the coupled modes that follows from the dynamical equations is given by

$$(1 - \omega^2/v_s^{02}k^2)(1 - i\omega/\Gamma_0) = T_c/T, \quad (6)$$

with T_c the critical temperature of the system, which is determined by the zero-frequency pole of the response functions as

$$k_B T_c = n_0 A^2/(\rho v_s^{02}), \quad (7)$$

whereas the full correlation functions for the pseudospin and phonon amplitudes that follow from Eqs. (5) are

$$\langle ss\rangle_{k,\omega} = (k_B T/\omega)\chi_s/(1 - k^2A^2\chi_Q\chi_s), \quad (8a)$$

$$\langle sQ\rangle_{k,\omega} - (k_B T/\omega)kA\chi_Q\chi_s/(1 - k^2A^2\chi_Q\chi_s), \quad (8b)$$

with $\langle QQ\rangle_{k,\omega}$ given by (8a) with $s \to Q$. The quasielastic scattering cross section is in turn given by a linear combination of the correlation functions.

Depending on the temperature and for a given coupling constant several interesting features emerge, as shown in Fig. 1, where we show the central-peak dispersion $\Gamma(k)$, i.e., the purely imaginary solutions of Eq. (6) as a function of k, for different temperature values. Three different regimes are worth discussing in some detail: (1) $T \gg T_c$. In this case the modes determined by Eq. (6) correspond to a purely imaginary excitation of width $\Gamma(k)$ and two complex modes located at the renormalized phonon frequencies. As shown in Fig. 1, curve a, the central-peak dispersion is weak and for $k = 0$ one obtains the unrenormalized width Γ_0. (2) $T = T_Z > T_c$. As the temperature is lowered further the acoustic phonons become overdamped and at T_Z a Z branch appears in which for a particular wave vector k_Z the three solutions of Eq. (6) become purely imaginary. The condition for the existence of a triple root of Eq. (6) gives T_Z as

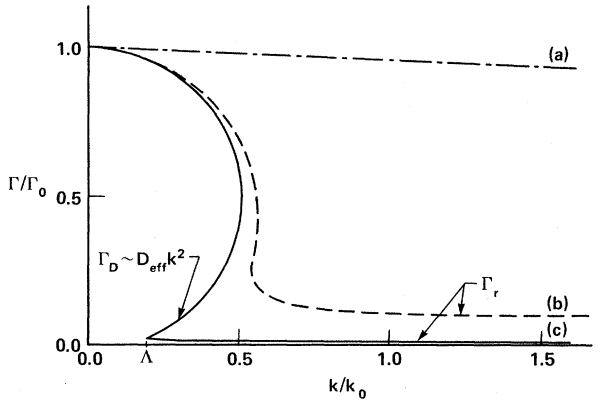

FIG. 1. Central-peak dispersion as the critical temperature T_c is approached from above. Curve a corresponds to $T = 10T_c$, curve b to $T = \frac{9}{8}T_c$, and curve c to $T = 1.01T_c$. The frequencies plotted are the purely imaginary solutions of Eq. (6) where $k_0 = \Gamma_0/v_s^0$. Other symbols are defined in the text.

$$T_Z = \tfrac{9}{8}T_c, \quad (9)$$

with k_Z given by

$$k_Z = 3^{-1/2}\Gamma_0/v_s^0. \quad (10)$$

For this particular value of the wave vector the central-peak width becomes $\Gamma_Z = \frac{1}{3}\Gamma_0$. As Fig. 1, curve b, also shows, the $k = 0$ value of Γ is still pinned at Γ_0. (3) As $T \to T_c^+$ for $k \simeq 0$, the sound velocity softens as $v_s^2 = v_s^{02}(T - T_c)/T$, and for large k the renormalized width becomes $\Gamma_r = \Gamma_0 \times (T - T_c)/T$ (see Fig. 1, curve c). In addition, a hydrodynamic branch starts to appear with $\Gamma(k)$ behaving like $\Gamma(k) \simeq D_{eff}k^2$, a reflection of the fact that the overdamped acoustic phonons provide a long-range interaction that leads to conservation of the pseudospin variable. The effective diffusion coefficient, which in the case of liquids corresponds to the shear mode diffusion,[14] is given by

$$D_{eff} = v_s^{02}/\Gamma_0. \quad (11)$$

This mode behaves as a diffusive hydrodynamic mode for a range of k greater than a lower cutoff $k_\Lambda = \Lambda k_0$, as illustrated in Fig. 1, curve c. Solu-

tion of Eq. (6) shows that for $T \to T_c$, $\Lambda \to 4\sqrt{3}(1 - T_c/T)$. The finite value of k_Λ for $T \neq T_c$ insures that the total pseudospin number is not strictly conserved. Of equal importance is that for $k \approx 0$ there still exists an unrenormalized relaxation rate Γ_0. This peculair behavior is a result of the interactions that we have been considering; i.e., an initially nonconserved variable that only through the renormalization of the coupling field acquires conserved characteristics. Finally, for $T \to T_c$, $\Lambda \to 0$ and the $k \approx 0$ central peak has contributions from the unrenormalized mode of width Γ_0, the hydrodynamic mode, and the component of width Γ_r whose integrated intensity behaves as $T/(T - T_c)$. The behavior of the quasielastic cross section for light scattering in the temperature range $T_c < T < T_Z$, is shown in Fig. 2, where we have taken the strain contribution to the dielectric fluctuations to be 10 times larger than that of the pseudospin variable.[2]

Here we mention two examples of systems that are described by a Hamiltonian of the form given by Eq. (2) and that display phase transitions which are quite close to being second order. The first such example is the superionic conductor $RbAg_4I_5$, which has a phase transition at a T_c of 208°K associated with partial ordering of the Ag ions.[15] The symmetry is lowered from cubic to rhombohedral. This involves the C_{44} elastic constant (which implies[12] $d^* = 3$), the softening of which has been observed.[16] We have previously shown[2] that from the ionic conductivity one estimates that $\Gamma_0 \approx 10^{10}$ Hz, and from ultrasonic attenuation,[16] one obtains $A \sim 0.1$ eV. Using $T_c = 208$°K and $v_s^0 = 1.7 \times 10^5$ cm/sec,[16] Eq. (7) leads to $A \sim 0.4$ eV. The agreement between these numbers indicates that acoustic phonons play a significant role in the order-disorder transition. The development of a Z branch at $T \sim \frac{9}{8} T_c = 234$°K would show that acoustic phonons dominate the critical dynamics. (The presence of other coupling mechanisms would depress T_Z nearer to T_c.) Since $\Gamma_0 \sim 10^{10}$ Hz and $k_Z \sim 3 \times 10^4$ cm^{-1}, quasielastic-light-scattering techniques appear appropriate to probe the central-peak behavior.

Another interesting possibility is provided by the doubly degenerate, crystal-field-split ground state of the Jahn-Teller solid $TmVO_4$, which shows a strong coupling to acoustic phonons with a nearly second-order phase transition at $T_c = 2.1$°K.[4-6] The elastic constant C_{66} measured at ultrasonic frequencies has been found to extrapolate to zero at T_c and to vary with magnetic field as expected from the coupling to the spin system.[6] It is also shown in Ref. 6 that the coupling to the acoustic phonons is even larger than indicated by the value of T_c because other spin interactions tend to inhibit ordering. Using the parameters from Ref. 6 in our formulas with χ_s replaced by a mean-field expression to include the other spin interactions,[6] we find a large range of anomalous dispersion, i.e., for $T_c < T < T_Z = 2.50$°K. Thus we expect the retarded phonon field to lead to a rich structure in the "central peak," in contrast to the simple narrowing independent of wave vector predicted in Ref. 5. In this system, the val-

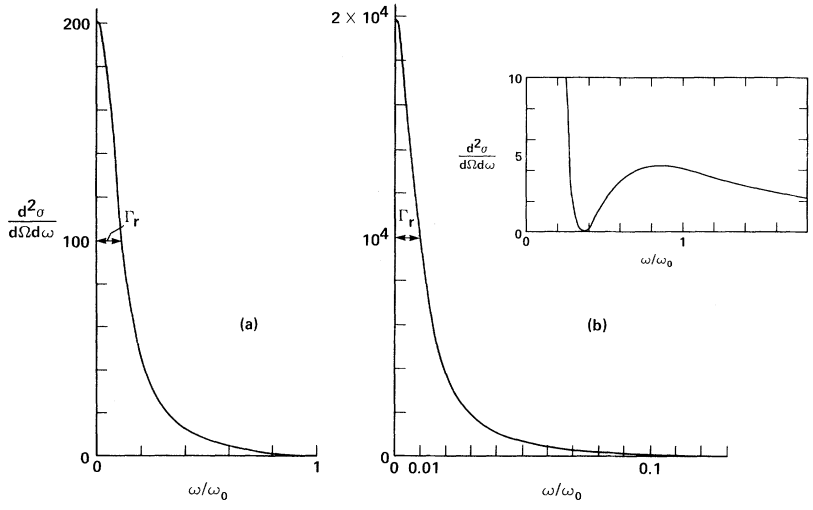

FIG. 2. The quasielastic cross section for light scattering in the regime $T_c < T < T_Z$ with $\omega_0 = v_s k$. (a) $T = 1.1 T_c$ and $k/k_0 = 1/\sqrt{3}$; (b) $T = 1.01 T_c$ and $k/k_0 = 0.3$. The inset shows interference effects at large values of ω/ω_0.

ue of Γ is not known[17] and, of course, Γ itself will vary over the wide range $T \leq 100°K$ in which C_{66} is renormalized.[6]

As we have shown, the critical dynamics of dense pseudospin systems interacting via long-range forces that are dynamic in nature shows very distinct features when compared to those which have nonretarded interactions. In particular, the evolution of an initially nonconserved variable towards hydrodynamic behavior gives rise to the appearance of a Z branch in the central-peak dispersion, together with the existence of an unrenormalized relaxation rate that persists throughout the critical temperature range. Although in realistic solids short-range interactions may also be present, the signature of the interactions that we have discussed is likely to persist and be observable by light-scattering techniques.

We wish to thank Professor Roger Elliot for pointing out to us the relevance of our study to Jahn-Teller systems and to $TmVO_4$ in particular. We have also profitted from useful discussions with Professor Shang-keng Ma and Professor Lu Sham.

[1]These degrees of freedom have been recognized as playing an important role in the central-peak problem of a number of solids, notably ferroelectrics. See, for instance, B. I. Halperin and C. M. Varma, Phys. Rev. B 14, 4030 (1976); see also P. A. Fleury and K. B. Lyons, Phys. Rev. Lett. 37, 1088 (1976).

[2]B. A. Huberman and R. M. Martin, Phys. Rev. B 13, 1498 (1976), and Bull. Am. Phys. Soc. 22, 302 (1977).

[3]T. Bischofberger and E. Courtens, Phys. Rev. Lett. 35, 1451 (1975).

[4]G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. 38, 1 (1975).

[5]E. Pytte, Phys. Rev. B 8, 3954 (1974).

[6]R. L. Melcher, E. Pytte, and B. A. Scott, Phys. Rev. Lett. 31, 307 (1973).

[7]H. D. Dardy, V. Volterra, and T. A. Litovitz, J. Chem. Phys. 59, 4491 (1973).

[8]See, for instance, Shang-keng Ma, *Modern Theory of Critical Phenomena* (Benjamin, Reading, Mass., 1976).

[9]Y. Yamada, H. Takatera, and D. L. Huber [J. Phys. Soc., London 36, 641 (1974)] have studied the central-peak behavior for Ising-like systems that represent some ferroelectric transitions.

[10]An excellent review is given by B. I. Halperin and P. C. Hohenberg, Rev. Mod. Phys. (to be published); see also H. Metiu, K. Kitahara, and John Ross, J. Chem. Phys. 65, 393 (1976).

[11]H. Wagner and H. Horner, Adv. Phys. 33, 587 (1974).

[12]J. Als-Nielsen and R. J. Birgeneau, to be published.

[13]A. Aharony, Phys. Rev. B 8, 3363 (1973).

[14]P. A. Egelstaff, *An Introduction to the Liquid State* (Academic, New York, 1967).

[15]M. B. Salamon, Bull. Am. Phys. Soc. 22, 249 (1977).

[16]M. Nagao and T. Kaneda, Phys. Rev. B 11, 2711 (1973); L. J. Graham and R. Chang, J. Appl. Phys. 46, 2433 (1975).

[17]In a similar system, $TbVO_4$, it has been concluded that $\Gamma \sim 10^{11}$ rad/sec at $T \sim 36°K$, so that the dispersion occurs in a range accessible by light scattering. See J. Sondercock *et al.*, J. Phys. C 5, 3126 (1972).

Magnetic "Tagging" of Superionic Conductors

R. D. Hogg, S. P. Vernon, and V. Jaccarino
Physics Department, University of California, Santa Barbara, California 93106
(Received 26 June 1977)

Introducing magnetic ions (e.g., Mn^{2+}) into a superionic conductor produces large temperature-dependent effects on the NMR linewidths. This makes possible the determination of the mobile species, hopping times of 10^{-3}–10^{-12} seconds, and the range of ionic motion In magnetically "tagged" PbF_2, comparison is made between experiment and theory for the various regions of temperature in which the hopping rate of the F^- ions is slow, comparable to, or fast, compared with the F^{19} transferred hyperfine interaction with the Mn^{2+} electronic spin.

With the increasing interest in superionic conductors,[1] more attention is being given to the microscopic character of ionic motion in the solid electrolytes. NMR has been a useful tool in this regard,[2] since the resonance linewidth, $\Delta\omega \equiv T_2^{-1}$, and spin-lattice relaxation rate T_1^{-1} are sensitive to the ion hopping rate τ_c^{-1}. Motional narrowing is observed when τ_c^{-1} becomes comparable with the nuclear dipolar broadening $(\Delta\omega)_d$ and a maximum in T_1^{-1} occurs when $\tau_c^{-1} = \omega_0$, the Zeeman frequency.

We demonstrate below that a variety of supplementary information (mobile ion, hopping rate, and range of motion) may be obtained in NMR