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The Calculation of Current Correlations in Classical Fluids via Modeled Kinetic Equations*

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The transverse and longitudinal current correlations in a simple classical fluid were originally calculated from a modeled kinetic equation using an approximate solution valid for only small values of wave number k. These correlation functions have been recalculated using the exact solution of this kinetic equation for arbitrary values of k.

Projection operator techniques can be used to derive an exact kinetic equation[1] describing the time correlations of fluctuations in the microscopic phase density for a classical many-body system. In a recent paper[2] (hereafter referred to as I) this kinetic equation was approximated using a modeling procedure and then applied to the calculation of current-current time correlation functions in simple classical fluids. In the notation of I, the Laplace-Fourier-transformed form of this modeled kinetic equation is

$$\left(s-\frac{i\vec{k}\circ\vec{p}}{m}\right)\tilde{\mathcal{G}}_k(\vec{p},\vec{p}\,'',s)+\frac{i\vec{k}\cdot\vec{p}}{m}M(\vec{p})\,nc(k)$$

$$\times\int d\vec{p}\,'\,\tilde{\mathcal{G}}_k(\vec{p}\,',\vec{p}\,'',s)=\mathcal{G}_k(\vec{p},\vec{p}\,'',0)$$

$$+\frac{D(0)}{s+\alpha(k)}\left(\frac{\partial}{\partial\vec{p}}\cdot\frac{\partial}{\partial\vec{p}}+\frac{\beta}{m}\frac{\partial}{\partial\vec{p}}\cdot\vec{p}\right)\tilde{\mathcal{G}}_k(\vec{p},\vec{p}\,'',s)$$

$$-\frac{\vec{p}M(\vec{p})\cdot\overleftrightarrow{\mathfrak{D}}(k)}{s+\alpha(k)}\circ\int d\vec{p}\,'\vec{p}\,'\tilde{\mathcal{G}}_k(\vec{p}\,',\vec{p}\,'',s). \qquad (1)$$

Hence providing one can solve this equation for $\tilde{\mathcal{G}}_k(\vec{p},\vec{p}\,'',s)$, it is a simple matter to compute the transverse and longitudinal current-correlation functions $\mathcal{J}_\perp(k,\omega)$ and $\mathcal{J}_\parallel(k,\omega)$ by merely taking suitable moments in momentum of this solution.

In I this solution was obtained in an approximate fashion by reducing (1) to an infinite heirarchy of equations for the moments of $\tilde{\mathcal{G}}_k(\vec{p},\vec{p}\,'',s)$ and then truncating this set to obtain the approximate solution. However, it was recently pointed out by Lebowitz, Percus, and Sykes[3] that equations such as (1) can be solved exactly by utilizing Fourier transforms in momentum $\vec{p}$. In the interest of completeness, we have recalculated $\mathcal{J}_\perp(k,\omega)$ and $\mathcal{J}_\parallel(k,\omega)$ using these exact solutions.

Following Lebowitz *et al.*,[3] one can solve equation (1) to find the cosine transform of the transverse current-correlation function as

$$\mathrm{J}_\perp(k,\omega)$$

$$=\mathrm{Re}\left[\lim_{s\to i\omega}\left(\frac{1+I(\kappa^2,z+1)}{s+[g(s)-h(s)]-h(s)I(\kappa^2,z+1)+\kappa^2g(s)}\right)\right], \qquad (2)$$

where, in the notation of Refs. 2 and 3,

$$I(\kappa^2,z)\equiv e^{\kappa 2}(\kappa^2)^{-(z+\kappa 2)}\int_0^{\kappa 2}dx\,e^{-x}x^{z+\kappa 2}, \qquad (3)$$

$$\kappa^2\equiv\frac{k^2}{m\beta}g^{-2}(s),\quad z\equiv\frac{s}{g(s)},\quad g(s)\equiv\frac{(\beta/m)D(0)}{s+\alpha(k)}, \qquad (4)$$

$$g(s)-h(s)=\frac{1}{s+\alpha(k)}\left(\frac{k^2C_{44}(k)}{mn}-\frac{k^2}{m\beta}\right). \qquad (5)$$

Similarly, solving for the longitudinal current-correlation function $\mathcal{J}_\parallel(k,\omega)$ yields

$$\mathcal{J}_\parallel(k,\omega)=(m\beta\omega^2/k^2)S(k,\omega), \qquad (6)$$

where the scattering law $S(k,\omega)$ is given by

$$S(k,\omega)=\mathrm{Re}\left[\lim_{s\to i\omega}S(k)\left(\frac{1+I(\kappa^2,z)-[f(s)/g(s)][zI(\kappa^2,z)-\kappa^2]\kappa^{-2}}{(\kappa^2+z)g(s)+[\kappa^2g(s)nc(k)-zh(s)][zI(\kappa^2,z)-\kappa^2]\kappa^{-2}}\right)\right] \qquad (7)$$

$$f(s)+g(s)=\frac{1}{s+\alpha(k)}\left(\frac{k^2C_{11}(k)}{mn}-\frac{3k^2}{m\beta}+\frac{k^2}{m\beta}nc(k)\right). \qquad (8)$$

It can be verified by straightforward calculations that these solutions reduce to our earlier approximate solutions [Eqs. (30), (47), and (48) of I] for small values of k.

The solutions can now be used to suggest suitable choices for the "relaxation parameter" $\alpha(k)$. In particular, note that $\mathcal{J}_\perp(k,\omega)$ must satisfy

$$\lim_{k\to 0}(k^2/mn)\mathcal{J}_\perp(k,0)=\eta_s^{-1}. \tag{9}$$

Using the form (2), this implies $\alpha(0)$ must satisfy

$$C_{44}(0)-\frac{n}{\beta}\left(1-\frac{\alpha^2(0)}{(\beta/m)D(0)}\right)=\eta_s\alpha(0) \; . \tag{10}$$

Further, recall[2] that for large k, $\mathcal{J}_\perp(k,\omega)$ must pass to the ideal-gas form

$$\mathcal{J}_\perp(k,\omega)\sim\left(\frac{\pi m\beta}{2k^2}\right)^{1/2}\left[1-\left(\frac{\omega^2}{k^2}\frac{m\beta}{2}\right)+\cdots\right] \; . \tag{11}$$

If we note that

$$I(\kappa^2,z+1)\sim(\tfrac{1}{2}\pi)^{1/2}\kappa-(z+1+\tfrac{2}{3})$$
$$+(\tfrac{1}{32}\pi)^{1/2}(2z^2+6z+1)/\kappa+O(\kappa^{-2}) \; , \tag{12}$$

then it is straightforward to verify that any choice of $\alpha(k)$ which behaves as $O(k^2)$ for large k will force (2) to satisfy the limit (11).

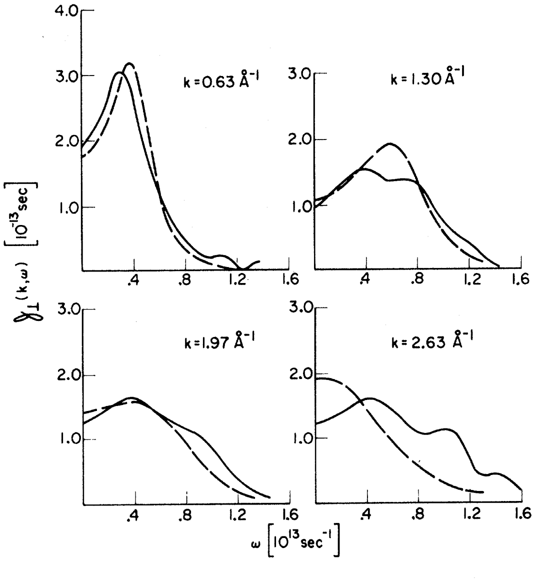

FIG. 1. The transverse current-current correlation function $\mathcal{J}_\perp(k,\omega)$ versus ω and k for argon. The solid curves represent the computer data of Rahman (Ref. 4), while the dashed curves represent the results obtained by solving the modeled kinetic equation.

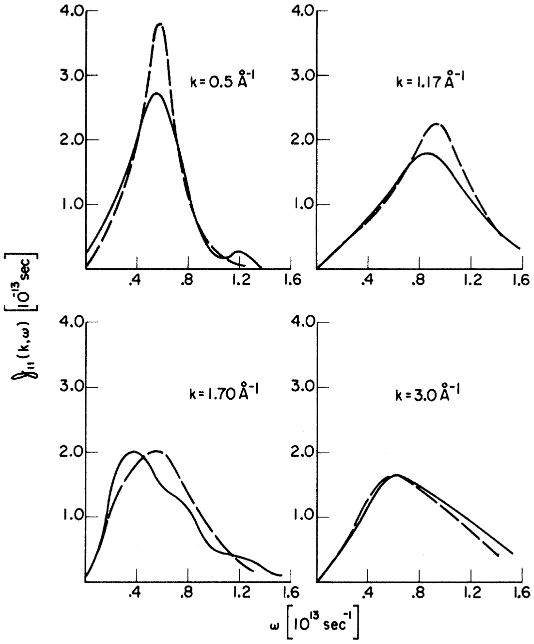

FIG. 2. The longitudinal current-current correlation function $\mathcal{J}_\parallel(k,\omega)$. Notation is similar to that of Fig. 1.

The corresponding analysis of $\mathcal{J}_\parallel(k,\omega)$ suggests a similar behavior for $\alpha(k)$. Hence any $\alpha(k)$ we choose must satisfy the constraints

$$\begin{aligned}&\alpha(k)\to\alpha(0)\quad\text{as}\quad k\to 0\;,\\&\alpha(k)=O(k^2)\quad\text{as}\quad k\to\infty\end{aligned} \tag{13}$$

to insure the correct large- and small-k behavior of $\mathcal{J}_\perp(k,\omega)$ and $\mathcal{J}_\parallel(k,\omega)$.

We have repeated the calculations of $\mathcal{J}_\perp(k,\omega)$ and $\mathcal{J}_\parallel(k,\omega)$, using the forms (2) and (7) for argonlike systems at $T=76$ °K, $\rho_0=mn=1.407$ g/cm^3, and compared these results with Rahman in Fig. 1 and 2. An interpolative model was chosen for $\alpha(k)$:

$$\alpha(k)=\alpha(0)[1+(k/k_0)^2] \; , \tag{14}$$

which satisfies both of the constraints (13). Here the interpolation constant was chosen as $k_0=1.5$ Å^{-1} (although the calculations appear to be rather insensitive to the value chosen for k_0). The agreement with the computer experiments of Rahman[4] is considerably improved over our earlier approximate solutions[2] of the modeled kinetic equations. These results reinforce our earlier conclusions concerning the usefulness of modeled kinetic equations such as (1) in the study of the dynamics of many-body systems in which large-frequency and short-wavelength information is desired (such as in inelastic neutron scattering from liquids).

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Phenomenological Model for ^{3}He near the Critical Point

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A modification of a previously discussed model for condensation in Fermi systems is applied phenomenologically to ^{3}He. The modified model contains an infinite sum of simple many-body interactions. Upon comparison of the model with experiment, good agreement is obtained for the exponents γ', β, and δ. The exponent α' describes a slightly stronger singularity than is observed, and the exponents γ and α retain their classical values.

In this note, we present a model offering a phenomenological description of the liquid-vapor phase transition in ^{3}He. The model is based on a certain modification of a model for phase transitions in Fermi systems developed by Gartenhaus and Stranahan[1,2] and further analyzed by Gartenhaus and the present author.[3,4] This earlier model is defined by the Hamiltonian

$$H=\sum_{\vec{k}} t(\vec{k})N_{\vec{k}}+(1/2\Omega)\sum_{\vec{k},\vec{q}} W(\vec{k},\vec{q})N_{\vec{k}}N_{\vec{q}}, \tag{1}$$

where $N_{\vec{k}}$ is the number operator for a fermion of spin and wave vector $\vec{k}$, $t(\vec{k})$ is the single-particle kinetic energy, $W(\vec{k},\vec{q})$ is the two-particle interaction, and Ω is the quantization volume. In the thermodynamic limit ($\Omega\to\infty$ particle density n fixed), the partition function for this model can be explicitly evaluated[5] and the thermodynamic properties of the model are summarized by the equation

$$n(\beta,\mu)=\sum_{\vec{k}} \rho_{\vec{k}}(\beta,\mu), \tag{2}$$

where n is the particle density, $\beta=1/k_BT$, μ is the chemical potential, and the single-particle density matrix $\rho_{\vec{k}}(\beta,\mu)$ satisfies the nonlinear integral equation

$$\rho_{\vec{k}}(\beta,\mu)=\{1+\exp\beta[t(\vec{k})+(1/\Omega)\textstyle\sum_{\vec{q}} W(\vec{k},\vec{q})\,\rho_{\vec{q}}-\mu]\}^{-1}. \tag{3}$$

By analyzing the solutions of Eq. (3), Gartenhaus and Stranahan[1,2] found that for a large class of interactions $W(\vec{k},\vec{q})$ a first-order phase transition occurs in the model. In a subsequent study,[3] it was found, regardless of the detailed form of the interaction $W(\vec{k},\vec{q})$, provided that certain smoothness criteria are satisfied, the critical exponents[6] associated with the model always assume the classical values.

The modification we wish to consider here consists of including an infinite series of simple many-body interactions in the Hamiltonian with coefficients chosen so that it can be written in the form

$$\begin{aligned}H=&\textstyle\sum_{\vec{k}} t(\vec{k})N_{\vec{k}}+P(\sum_{\vec{k}}N_{\vec{k}}/\Omega)\\&+[\lambda/(x+1)]\textstyle\sum_{\vec{k}}|N_{\vec{k}}/\Omega-n_c|^{x+1},\end{aligned} \tag{4}$$

where P is a polynomial in the operator $\sum_{\vec{k}}N_{\vec{k}}/\Omega$ and λ, x, and n_c are unspecified constants. If we now assume that in the thermodynamic limit the partition function associated with this new Hamiltonian can again be evaluated by the method of Girardeau, the single-particle density matrix for the new model becomes

$$\begin{aligned}\rho_{\vec{k}}(\beta,\mu)=\{1+\exp\beta[&t(\vec{k})+P'(n)\\&+\lambda(n-n_c)|n-n_c|^{x-1}-\mu]\}^{-1},\end{aligned} \tag{5}$$

where $P'(n)$ is the derivative of the polynomial P in Eq. (4). It has then been shown[3,4] that $P(n)$ can be chosen so that a phase transition does occur in the model[3,4] and the resulting critical exponents are given as functions of x in Table I. In order to obtain these values, we have set n_c equal to the critical density and assumed $k-1<x<k$, k being the order of the lowest nonvanishing derivative of the chemical potential μ with respect to n at the critical point.[7] For the case $\lambda=0$, the critical exponents again assume the classical values.[3]

We turn now to the application of this nonclassical model to the liquid-vapor critical region of ^{3}He. The properties of ^{3}He near the critical point have been the subjects of several recent experiments[8–12] and a summary of the experimental